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AFWAL-TR-88-2049



MODERN MULTIPLE-PULSE, HIGH FIELD NMR STUDIES OF HIGH DENSITY JET FUELS

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AUGUST 1988

FINAL REPORT FOR PERIOD JUNE 1986 - MAY 1988

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UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

Form Approved
OMB No. 0704-0188

REPORT DOCUMENTATION PAGE					
1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		1b. RESTRICTIVE MARKINGS			
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited.			
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) AFWAL-TR-88		5. MONITORING ORGANIZATION REPORT NUMBER(S) AFWAL-TR-88-2049			
6a. NAME OF PERFORMING ORGANIZATION Dept. of Chemistry & Fuels Engineering, Univ. of Utah	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Aero Propulsion Laboratory (AFWAL/POSF) Air Force Wright Aeronautical Lab			
6c. ADDRESS (City, State, and ZIP Code) Salt Lake City, Utah 84112		7b. ADDRESS (City, State, and ZIP Code) Wright-Patterson AFB OH 45433-6563			
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Air Force Wright Aeronautical Lab	8b. OFFICE SYMBOL (If applicable) AFWAL/POSF	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F33615-86-C-2643			
8c. ADDRESS (City, State, and ZIP Code) AFWAL/POSF Wright Patterson AFB OH 45433-6563		10. SOURCE OF FUNDING NUMBERS			
		PROGRAM ELEMENT NO. 61101F	PROJECT NO. ILIR	TASK NO. P6	WORK UNIT ACCESSION NO. 16
11. TITLE (Include Security Classification) MODERN MULTIPLE-PULSE, HIGH FIELD NMR STUDIES OF HIGH DENSITY JET FUELS					
12. PERSONAL AUTHOR(S) D.W. Alderman, J.C. Curtis, D.M. Grant, C.L. Mayne, and Ronald J. Pugmire					
13a. TYPE OF REPORT Final	13b. TIME COVERED FROM 09JUN86 TO 06MAY88	14. DATE OF REPORT (Year, Month, Day) August 1988		15. PAGE COUNT 51	
16. SUPPLEMENTARY NOTATION This research was partially funded by the in-house independent research fund.					
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) high field NMR, 2D NMR, proton NMR, carbon-13 NMR, fuel analysis, JP-4, JP-5, pattern recognition, FT-NMR, structural identification.			
FIELD 21	GROUP 04				
21	05				
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Modern high field NMR spectroscopic techniques have been evaluated in order to assess the capabilities of such techniques for the study of jet fuels and related materials. The utility and quantitative aspects of spectral editing techniques were evaluated. The DEPT method is one of the more attractive spectral editing pulse sequences but the quantitative aspects of all such editing procedures are quite poor.					
The field of 2-dimensional NMR spectroscopy is growing rapidly and several existing 2-D techniques are quite attractive for jet fuel studies. The protonhomonuclear correlation experiment is shown to provide useful information even in complex fuels. The heteronuclear correlation (¹ H- ¹³ C) experiment permits one to sort out overlapping lines in both the proton and carbon frequency domains. The J-coupled 2-D experiment is very useful for characterizing the nature of the carbon resonances as C, CH, CH ₂ and CH ₃ groups in jet fuels. A combination of heteronuclear correlation and J-coupled 2-D experiments allow one to sort and identify the hundreds of resonance lines in jet fuels. The 2-D inadequate method was shown to be a particularly useful experiment for determining carbon-carbon connectivities. A combination of the heteronuclear correlation, J-coupled, and INADEQUATE 2-D experiments proved to be a very powerful combination of techniques for identifying all of the major structural types of fragments in the JP-4, JP-5, and MIG-25 fuels. It is shown that pattern recognition techniques can be used to correlate the data from several experiments and identify fuel constituents at a level of detail that exceeds other presently available analytical methods.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED		
22a. NAME OF RESPONSIBLE INDIVIDUAL 2D LT JEFFREY L. MOLER			22b. TELEPHONE (Include Area Code) (513) 255-3549		22c. OFFICE SYMBOL AFWAL/POSF

I. INTRODUCTION

A. General Background.

Several critical areas of science and technology need to be advanced in the near future to maintain and strengthen the position of economic leadership of the United States. One area is the development of high speed aviation technology. Indeed, the United States must quickly address the technical issues concerning the viability of future, high-speed commercial and military aviation or face the possibility of losing its edge over foreign competitors together with associated strategic and security consequences. One of the basic issues facing the development of high-speed aircraft is the need for advanced fuels different in chemical composition and superior in properties as compared with currently used jet fuels.

Conventional jet fuels are required to have certain physical and chemical characteristics as outlined in their specifications. With regard to high speed flight, neither the current Jet A nor current JP-4 and JP-5 specifications will be adequate for fuels needed for sustained supersonic flight. At flight speeds above Mach 3, the fuel must withstand high liquid temperatures in the fuel system prior to introduction into the engine. If, at these temperatures, the fuel decomposes to form deleterious deposits, the heat transfer surfaces, fuel nozzles, and other components in the fuel system might be affected in a manner causing serious damage to the aircraft fuel system and engine. Thus, future fuels will be required to have physical properties dictated by the particular application and the temperatures to which it will be exposed.

The relationship between the properties of a fuel and its chemical constituents is not well known. While it is known empirically that certain classes of compounds can either enhance or degrade aviation fuel properties (e.g., aromatics increase soot formation, paraffins raise the freeze point, and naphthenes raise the volumetric heat of combustion), detailed correlation of chemical structure with physical properties is not yet possible. Since specification and perhaps tailoring of fuel properties is an integral part of engine design, a more complete knowledge of and, consequently, control over fuel characteristics is highly desirable. The concept of tailoring a fuel to a specific mission (dial-a-fuel concept) can only be achieved if we thoroughly understand the

molecular structural features that contribute to specific physical properties of hydrocarbon compounds in pure form as well as in mixtures. Only recently have combustion engineers begun to include chemical and physical properties in advanced models.

Fortunately, modern analytical techniques and data correlation methods offer tremendous potential for acquiring highly detailed chemical structural information. Modern NMR spectroscopic techniques in particular provide a very powerful method for determining the detailed chemical structure of complex materials.

B. Background on the Application of NMR Spectroscopy to Fuel Analysis.

NMR spectroscopy, initially of hydrogen and more recently of carbon has for many years been one of the major techniques for obtaining structural information on complex hydrocarbon mixtures. Essentially all the NMR work has been done with one-dimensional, "conventional" spectra. Analyses have been based on determining the intensity associated with various spectral regions which, by analogy with model compounds and mixtures, could be reasonably assigned to the desired structural components.

The most common of such analyses is the determination of an aromatic/aliphatic ratio. More refined analyses attempt to distinguish monocyclic from polycyclic aromatics, alpha and/or beta naphthenic hydrogens from straight chain aliphatics, etc. We have found results of such analyses to be quite useful. The utility of such rather gross structural distinctions in addressing subtle problems is, however, somewhat limited. Decisions as to which regions of a spectrum should be assigned to certain structural components are not always straightforward. For example, it is commonly assumed that aromatic hydrogen signals below 7.3 ppm arise from monocyclic aromatic compounds. This can be a reasonable assumption if, and only if, the sample does not contain compounds such as aromatic heterocycles or benzoic acid derivatives, which give signals above 7.3 ppm, or polycyclic phenols, which give signals below 7.3 ppm. The situation becomes even worse for the aliphatic region of the spectrum. For example, beta naphthenic CH_2 groups and aromatic CH_3 groups appear in the same region of the spectrum and ring protons in alicyclic compounds can occur in regions of the spectrum usually assigned to methyl signals.

Hence, the NMR analytical methods in use today are generally useful, but provide only rather gross structural distinctions and are frequently subject to considerable uncertainty with regard to some types of structural detail. This uncertainty is particularly aggravated for naphthenic materials such as are found in high density advanced jet fuels. Since the distribution of carbon between CH, CH₂, and CH₃ structural moieties has a profound effect on the physical and chemical properties of the fuel, it is imperative that reliable methods be developed for characterizing fuels..

C. New Spectroscopy Developments.

In view of the difficulties described above, it is useful to consider the present state-of-the-art NMR analytical capabilities. Over the past few years, a multitude of new pulse FT NMR experiments have been developed and applied to a variety of structural problems.^{1,2,3} These techniques can be loosely divided into two groups; spectral editing experiments and two-dimensional experiments.

Spectral editing experiments characterized by acronyms such as GASP, APT, INEPT, DEPT, and SEMUT provide several new options.^{1,2,3,4} All of them permit an unambiguous distinction between different structural components such as CH₃, CH₂, CH and nonprotonated carbons, obviously offering the potential to resolve some of the problems noted above. It is frequently possible to obtain a spectrum containing *only* signals from a specific type of carbon, for example, only nonprotonated carbons. This approach has two obvious advantages; only one type of structural feature is examined and the spectrum is greatly simplified since the other signals are absent. In a more sophisticated form, those experiments based on J selectivity (in which the presence, absence, or attenuation of a signal depends on the magnitude of the H-H and C-H coupling constants) provide the opportunity to obtain spectra from specific structural groupings, for example, aromatic CH groups located next to a sulphur or a nitrogen (potential markers for thiophenes, pyridines, quinolines, etc.), or specific CH₂ groups next to oxygen, nitrogen, or aromatic rings. Clearly, such experiments offer the opportunity to obtain much more specific qualitative and quantitative information about a complex sample than can be accomplished with the



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conventional techniques. Several of these techniques provide enhanced signal/noise vs. time, thus, reducing the time required to obtain information.

Two-dimensional NMR experiments acquire two (or more) kinds of information simultaneously and display this information as a two-dimensional matrix. The most common such experiment provides correlation information and is known as a COSY experiment. In a heteronuclear correlation experiment, one axis of the 2-D plot represents hydrogen chemical shifts while the other represents carbon chemical shifts. The homonuclear correlation experiment shows which hydrogen signals are coupled to each other (and, hence, represent hydrogens which are near to each other in structural components). Such experiments permit the ready identification of groupings such as CH_3CH_2- , $\text{CH}_3\text{CH}-$, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}=\text{CH}-$, etc. Heteronuclear correlation experiments are more useful because carbon chemical shifts are 20 times greater than hydrogen chemical shifts. As a result a group of signals, for example several CH_2 signals which all overlap in the hydrogen spectrum, are "sorted" or "separated" in the second or carbon dimension. Extraction of a spectral "slice" at a given carbon chemical shift permits observation of the proton signals without any interference from what would have been seriously overlapping signals in the hydrogen spectrum. Hundreds of such "individual component" spectra can be obtained from a single 2-D experiment. The procedure can be reversed to provide separate carbon spectra from materials whose carbon signals overlap, but whose hydrogen spectra are well resolved.

More sophisticated 2-D experiments present correlations between hydrogens and carbons separated by several bonds (RELAY experiments), establish carbon-carbon connectivities (INADEQUATE experiments^{3,4,5,6}), or provide specific spatial information such as distances and interatomic angles (NOE experiments). All such 2-D experiments, particularly when used together on the same sample, provide a heretofore unattainable ability to identify and quantify components of complex mixtures. Two-dimensional J-spectra were originally designed to provide coupling pattern information. In this context they can be used as a sort of 2-D editing technique to readily sort and distinguish carbons of different multiplicities or with different coupling constant values.

The above described experiments provide a massive amount of very specific experimental data. The nature and quantity of information is such that an investigator cannot fully interpret the data without the aid of computer algorithms designed for specific spectral interpretation functions. Only within the past year has commercially available technology been announced that would permit the investigator to acquire, store, and interpret the large spectral data files generated by advanced spectroscopic techniques.

II. GOALS AND OBJECTIVES OF THIS STUDY

When the project was first formulated (in 1985) a specific set of objectives was established.

These objectives were:

1. Evaluate the qualitative utility of using new pulse techniques for identifying specific structural units in complex mixtures such as jet fuels.
2. Evaluate the quantitative aspects of multiple-pulse spectral editing techniques.
3. Apply appropriate NMR techniques to standard jet fuels and high density jet fuels to be developed in order to increase the knowledge base of the components and structural units contained in these fuels.

To achieve these objectives, it was necessary to evaluate the qualitative as well as the quantitative aspects of the proposed experiments on model compounds and mixtures of model compounds. This approach permitted appropriate calibration and assessment of the new NMR techniques on materials that could be readily interpreted.

Some of the details of the original objectives changed slightly. These changes occurred in an evolutionary fashion as new information and advanced experimental techniques emerged. In the later stages of the work, it became apparent that sophisticated pattern-recognition methods must be developed to fully utilize the experimental data we had obtained. Hence, computer assisted pattern-recognition became a major effort in the later stages of the research.

III. OVERVIEW OF METHODS AND PROCEDURES

A. Exploration of Different Types of Experiments

The research was divided into three basic categories: (1) calibration and evaluation of techniques; (2) data transfer and processing; and (3) characterization of mixtures.

1. Calibration and Evaluation of Techniques

Calibration and evaluation of techniques were carried out with pure compounds. In view of the long range objectives of characterizing jet fuels, we selected a number of naphthenes from the API Standard Reference Materials at Carnegie-Mellon University. These highly purified materials are unique for many compounds of interest and are of known isomeric form; e.g. cis and trans forms for alkyl substituents. We evaluated the various spectral editing pulse sequences such as APT, INEPT, DEPT SEMUT² and GASP³ in order to assess their qualitative usefulness as well as their quantitative features. The various editing techniques impose some trade-offs in order to determine optimum experimental parameters. For example, INEPT experiments provide greater signal to noise in less time, but do not yield signals from nonprotonated carbons and are sensitive to differences in the C-H coupling constants. APT spectra (which are also sensitive to the C-H coupling constant value) do give signals from nonprotonated carbons, but provide less signal to noise improvement in a given time. However, DEPT and SEMUT experiments are relatively insensitive to the magnitude of the C-H coupling. We felt that the DEPT technique was satisfactory for a detailed study of quantitative accuracy as it represents a useful representation of the other spectral editing techniques.

Two-dimensional studies take more time than one-dimensional spectra. The amount of information potentially available is substantially greater and careful consideration was given to proper selection and optimization of these experiments. Proton homonuclear correlation experiments are performed most rapidly, but owing to the low dispersion of proton chemical shifts coupled with the extreme complexity of the fuel samples, these experiments are less likely to provide substantial amounts of useful information. Heteronuclear correlation and 2-D J-spectra offer the greatest potential for information content versus time involved and a major effort was

devoted to assessing the value of the data obtained versus time and resolution considerations. Heteronuclear 2-D J-spectra provide the same ability to differentiate CH₃, CH₂, CH, and nonprotonated carbons as do the spectral editing techniques. Since the coupling is displayed directly, they also offer the same opportunities as do the J-selective techniques. Dispersion of the signals into the second dimension also helps to reduce overlap in crowded spectral regions.

The value of ²H resonance experiments was noted early in this study. Modern high field spectrometers now offer the potential for spectral characterization of very complex materials using natural abundance deuterium as the molecular probe. The low natural abundance (0.0156%) precludes the troublesome clutter produced by ¹H-¹H coupling in proton NMR spectroscopy. A substantial amount of ²H NMR data was obtained and analyzed on 20 naphthenic model compounds to derive a set of spectral parameters that can be used to predict molecular structure and geometrical conformation in naphthenic materials.

Following a preliminary assessment of spectral editing and 2-D techniques of single compounds, carefully prepared mixtures of model compounds were studied. The multiple quantum INADEQUATE experiment permitted us to identify all of the 15 lines in a four component mixture and correctly assign the carbon-carbon bond connectivity. The homonuclear correlation experiment also permitted us to correlate and interpret data coming from individual components in the mixture. The phase sensitive INADEQUATE experiment was used to describe the model naphthene 1,1-dimethyl-tetralin as well as three jet fuels.

IV. RESULTS AND DISCUSSION

This section contains a summary of the experimental results obtained during the course of the project.

A. Data Transfer From Spectrometer to VAX

The goal of this section of the program has been to overcome the limitations on 1D and 2D NMR data set size imposed by the commercially available equipment. Large data sets are necessary to exploit the full resolution of the spectrometer. It is often possible to produce 0.25 Hz resolution over the 25-KHz spectral width necessary to cover a carbon-13 chemical shift range of 200 ppm. Digitization of this spectrum would require 100,000 points to put even a single point in a peak. Since four or more points are necessary to faithfully represent a peak such resolution calls for data set sizes in excess of 400,000 points. These are beyond the capability which manufacturers are currently delivering even for 1D spectra. The problem becomes especially severe for 2D spectra where the manufacturers limit data sets to much smaller sizes in both dimensions.

To overcome these limitations we have been working on involving our VAX 11/750 in the data acquisition and analysis process.

First, we are building hardware to allow accumulation of NMR FID's directly in the VAX. We are constructing a 32-M bit/sec serial link system which will employ emitter coupled logic and balanced shielded cable to carry FID data from the vicinity of the spectrometer magnet where it is generated to the VAX. The design of the hardware is complete and it is currently being constructed by the Chemistry Department Electronics Laboratory. The memory necessary to store and process this data on the VAX has been purchased and installed. The high speed, high resolution analog to digital converters necessary to digitize the FID's at the spectrometer have not been purchased.

Second, we have been developing the data handling software on the VAX. Pulsed NMR data is in the form of free induction decays (FID's) produced by the spectrometer. The FID's must be Fourier transformed, and in the case of two-dimensional (2D) NMR transposed and Fourier transformed a second time. The data must then be displayed for interpretation by the scientist.

These capabilities are now fully developed on our VAX 11/750 where we can process, display and analyze one-dimensional data sets up to 512 K (512 x 1024) complex points in size. We can presently process 2D data sets up to 8M (8 x 1024 x 1024) complex points in size, and thus do, for example, 64 K by 128 data sets. We can display sections of these large data sets up to 1024 by 1024. Our goals, which should be achieved soon, are 1 M complex point 1D data sets and 16 M complex point 2D data sets. The display software employs the color graphics system and a pair of Mouse Systems mice on the VAX.

B. Evaluation of the DEPT Technique

Investigations were made into the feasibility of using nuclear magnetic resonance (NMR) spectroscopy as a tool for quantitatively analyzing mixtures of aliphatic compounds. The ultimate goal would be to develop an analytical NMR technique that is capable of determining the identities of compounds in a complex mixture in a quantitative fashion.

The first stage of the project involved acquiring some standard, non-quantitative (i.e., using a pulse sequence that doesn't compensate for nuclear Overhauser effects) ^{13}C NMR spectra of ternary mixtures of methyl cyclohexanes. The sample was prepared analytically, measuring the weights of the 3 methyl cyclohexane components to the nearest milligram on an analytical balance. The sample was prepared under a vacuum and degassed using three freeze-pump-thaw cycles to eliminate as much atmospheric oxygen (a paramagnetic molecule) from the sample as possible. The ^{13}C NMR spectrum of this sample was then digitally integrated to obtain the relative concentrations of the compounds and compared with the known amounts. This data gives an average error of 13.7 percent relative to the known concentrations.

Finally, the feasibility of using the pulse sequence DEPT as a technique for analyzing mixtures was explored. DEPT is a specialized NMR pulse sequence that transfers magnetization from protons to adjacent carbon atoms.⁷ The advantage of using the DEPT experiment to analyze complex mixtures is that complicated spectra can be greatly simplified. The pulse sequence differentiates between different types of carbon nuclei (those carbon atoms bonded to 1 proton, 2 protons, or 3 protons), resulting in three relatively simple spectra as opposed to one complicated

spectrum. The DEPT pulse sequence is also a powerful qualitative analytical tool because it can differentiate between primary, secondary, and tertiary carbon atoms in a complex aliphatic mixture.

The DEPT experiment was performed on the methyl cyclohexane sample described above. Integration of the spectrum gave an average error of 29.2 percent relative to the known concentrations. This result suggests that the DEPT experiment as an analytical tool is not as accurate as other more conventional ^{13}C NMR techniques.

C. 2-D J Spectra and Heteronuclear Correlation Spectra

This section and the next one explain briefly the techniques used and summarize the structural information obtained from three aviation fuel samples (MIG-25 fuel, JP-4 fuel, and JP-5 fuel). Figures 1 and 2 show the standard one-dimensional proton and carbon spectra of the three samples. All three samples have very low aromatic content; thus, in what follows, attention will be concentrated on the aliphatic region of the spectrum. All of the proton signals are concentrated within a 2-ppm range, and there is little differentiation of the signals. The carbon spectrum, on the other hand exhibits an amazing amount of structure. Several hundred individual resonances can be distinguished in each spectrum. The challenge is to extract from this obviously information-rich data the desired structural information. Considerable progress can be made in this direction using two-dimensional NMR techniques as follows:

Heteronuclear J-coupled spectra allow determination of the number of protons attached to each carbon. The proton-carbon bonds can be established using a proton-carbon correlation experiment, and accurate proton and carbon chemical shifts can be obtained even in crowded areas of the spectrum. The phase-sensitive, 2-D INADEQUATE experiment (see the following section) detects carbon-carbon bonds which allows us to define the skeleton of a molecule or molecular fragment. Correlating the data from all of these NMR experiments can provide a detailed description of molecules or at least molecular fragments even in a complex mixture. Due to the insensitivity of NMR techniques compared to many other analytical methods, large amounts of sample are generally required to do the analysis; however, essentially unlimited amounts of sample are often available of fossil fuel liquids.

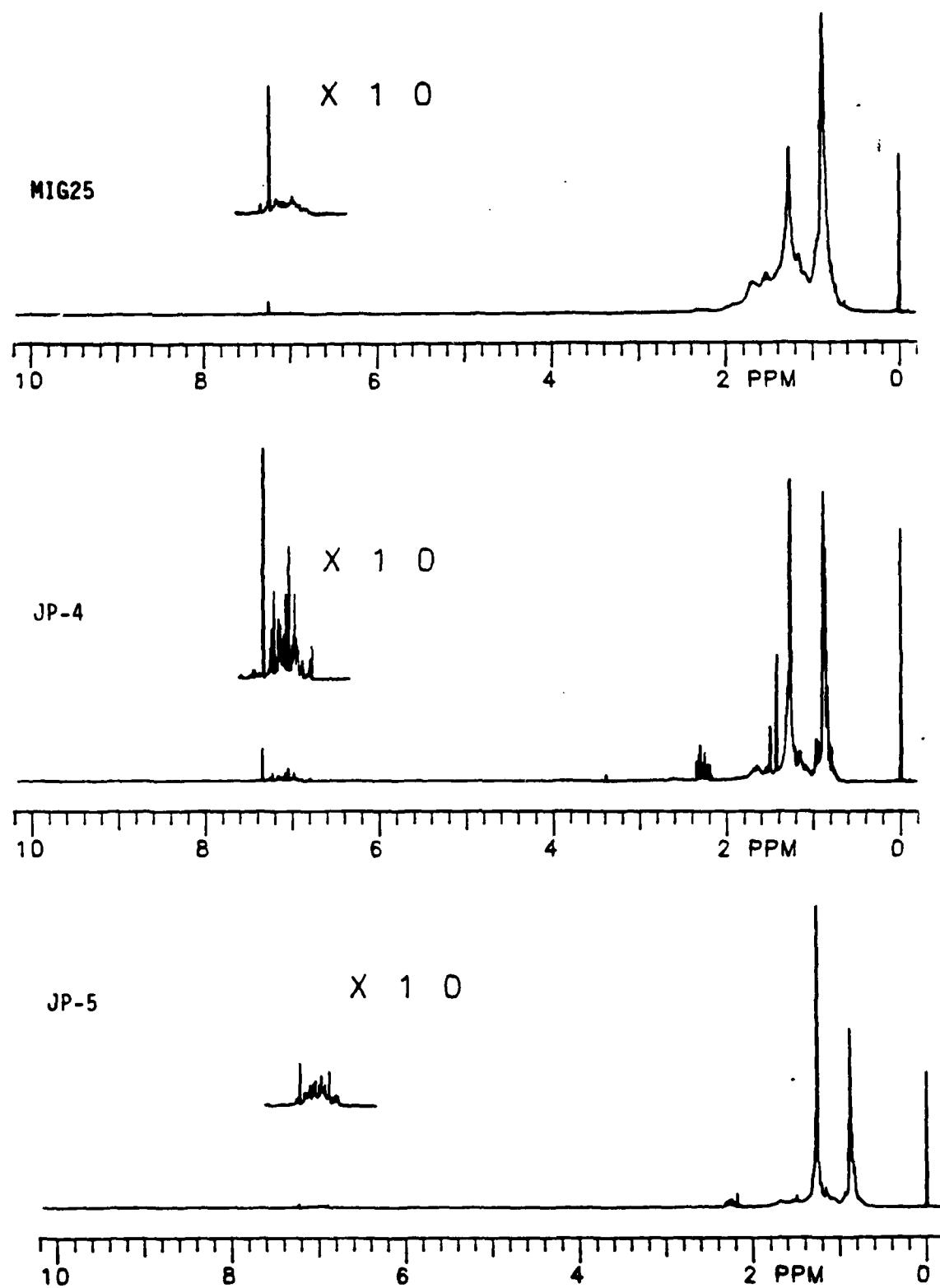
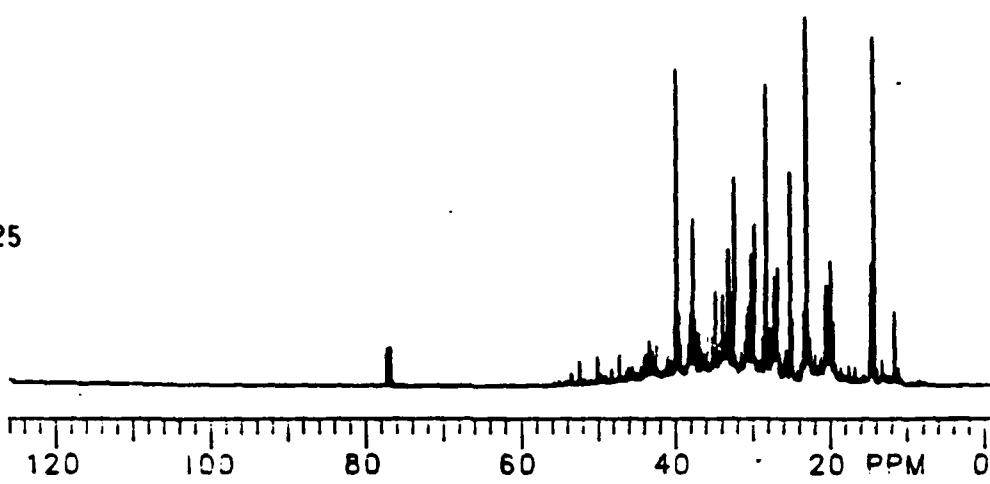
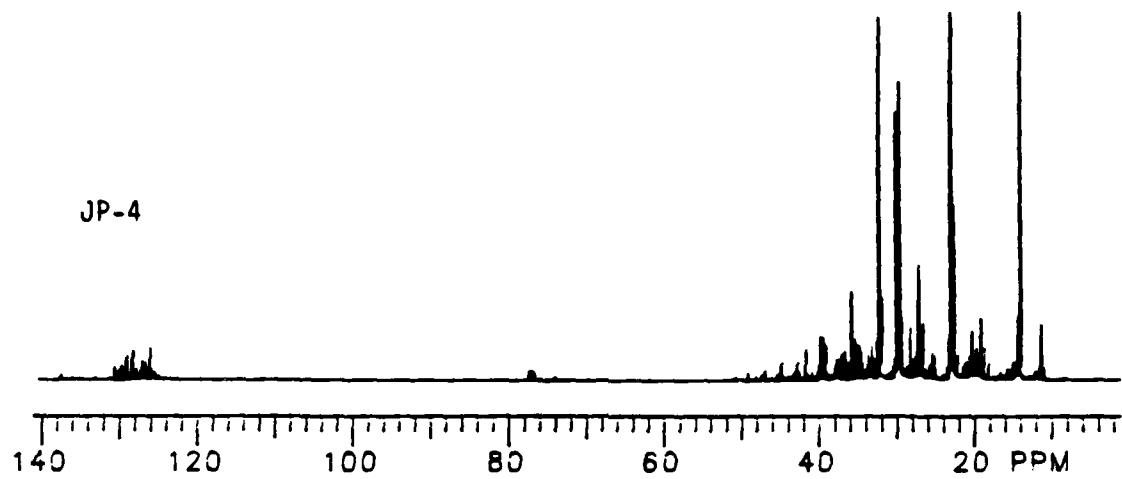


Figure 1: Proton spectra of three aviation fuels. Chemical Shifts are relative to TMS.

MIG25



JP-4



JP-5

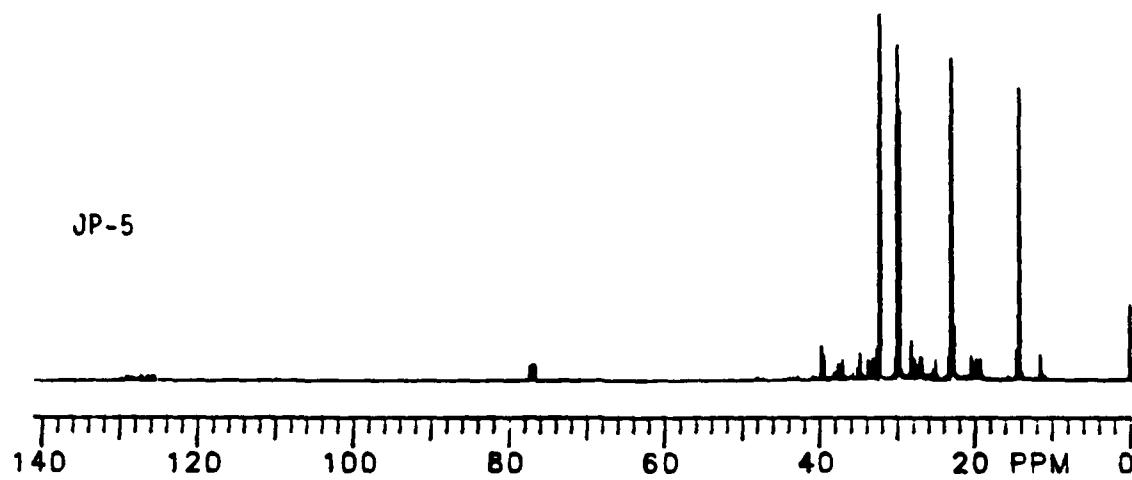


Figure 2: Carbon spectra of three aviation fuels. Chemical Shifts are relative to TMS.

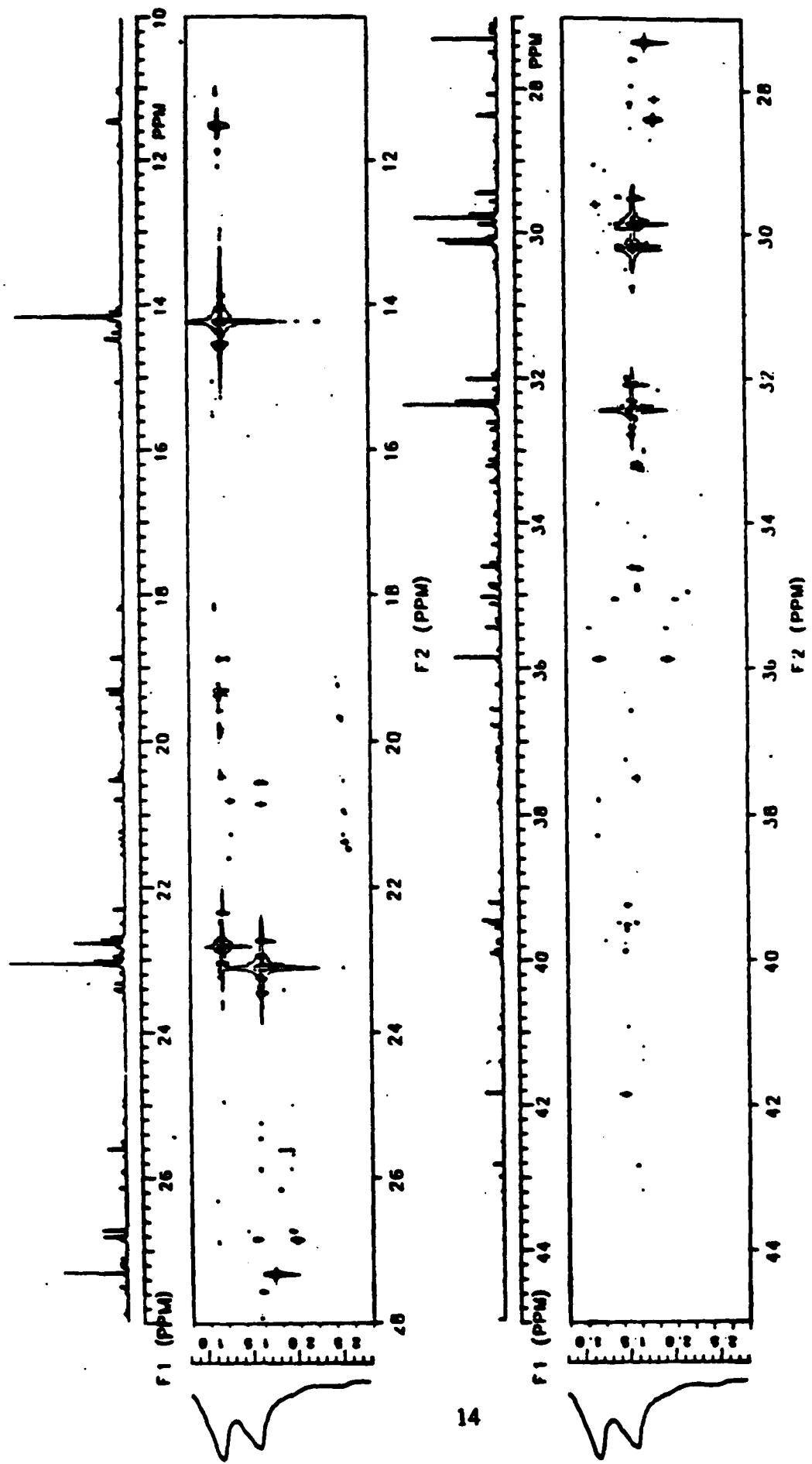


Figure 3: Contour plot of a proton-carbon-13 correlation spectrum of JP-4 fuel with 20% deuteriochloroform added as a lock solvent. The F_1 axis gives proton chemical shifts; the F_2 axis gives carbon-13 chemical shifts. Each peak in the contour plot indicates that protons having chemical shift F_1 are directly bonded to a carbon with shift F_2 . The proton and proton decoupled carbon-13 one-dimensional spectra are given along the respective axes for reference. All chemical shifts are with respect to TMS.

Correlation and J-spectra of the JP-4 fuel are presented as an example of the experiments; however, it is impossible to portray the spectra on paper in a very satisfactory way. The summaries of structural data presented later were actually obtained by using a color graphics system to carefully examine the data in expanded form using both contour maps and various slices and projections of the data. Figure 3 shows a carbon-proton correlation spectrum. One striking feature of this spectrum is that, even though the proton spectrum is quite featureless, accurate chemical shifts for various protons attached to carbon are obtainable from the 2D map. Conversely, there are many cases where carbon chemical shifts are nearly identical, but differing proton shifts serve to separate the resonances in the 2D map. Furthermore, the intensities of the peaks are at least roughly proportional to those of the carbon peaks shown in the one-dimensional spectrum along the top of the contour map. Due to time constraints the quantitative aspects of this data have not been fully investigated; but it should be possible to integrate regions of the contour map to obtain far more detailed information as to the concentration of various fragments than would be available from either the proton or the carbon spectrum alone. It is well known that peak intensities which accurately represent the concentrations of various components are very difficult to obtain in 2D spectra. However, pulse sequences can be designed to alleviate many of these problems, and some of them are amenable to mathematical corrections. We intend to explore just how accurately we can quantify the various spectral features.

Figure 4 shows a carbon proton 2-D J-spectrum of the JP-4 sample. Each carbon resonance shows a multiplet indicating how many protons are directly bonded to it. Using this data each resonance in Figure 3 can be assigned as a methyl, methylene, methine, or quaternary carbon. In some cases the weaker outer lines of a quartet or triplet do not show in the figure, but examination of individual cross sections of the data on a CRT display is usually sufficient to resolve the question. This serves to emphasize the necessity of developing methods for carefully analyzing each data set with as much aid from pattern recognition and statistical techniques (see section F) as possible. Note also that in some cases carbons with nearly identical chemical shifts are separated because of their differing multiplicities. The data extracted from these spectra and

similar ones for each of the other samples is accumulated in Tables 1 through 3. At this point a major fraction of the material in the sample has been categorized into CH_n fragments. The next step is to assemble as many as possible of the fragments into larger fragments or into molecules using the carbon-carbon connectivity information. This is the subject of the next section.

D. Carbon-Carbon Connectivities

The 2D INADEQUATE experiment provides direct information as to the carbon skeleton of a molecule. No other NMR experiment does this in such a clean, unambiguous way. However, the price of this information is very high. The natural abundance of C^{13} is 1.1 percent, and the experiment relies on observation of the 0.012 percent of molecules which have two adjacent carbon-13's. Thus, the sensitivity of the experiment is very poor, and it can be attempted only in cases where gram amounts of sample are available. Additionally, the experiment puts unusually high demands on the performance characteristics of the spectrometer. As an illustrative example, Figure 5 shows a series of traces parallel to the F2 axis of a spectrum of 1,1-dimethyltetralin. Each carbon-carbon bond in the molecule is characterized by an AX or AB spin system. (Protons are decoupled.) Resonances from molecules with only one carbon-13 or two non-adjacent carbon-13's are suppressed. Some residual signal from the two hundredfold more intense resonances from isolated carbon-13's is present, but can easily be distinguished from the characteristic plus-minus doublets of the AX system. Figure 6 illustrates schematically how each pair of bonded carbons produces a four line AX pattern displaced in the F1 dimension by the double quantum frequency (DQF). Each trace of Figure 5 is extracted from the full data set at the DQF corresponding to the appropriate bond. Figure 7 shows a contour plot of the phase sensitive 2D INADEQUATE spectrum of the JP-4 sample. From this spectrum and those in section C and similar sets for each of the other samples Figures 8 through 10 were compiled showing a set of fragments present in each sample. Table 4 lists the bonds making up the various fragments for the JP-5 fuel with references to Table 3 for the correlation and multiplicity information. The information is much more complete for the JP-5 sample because it was the last one to be done, and

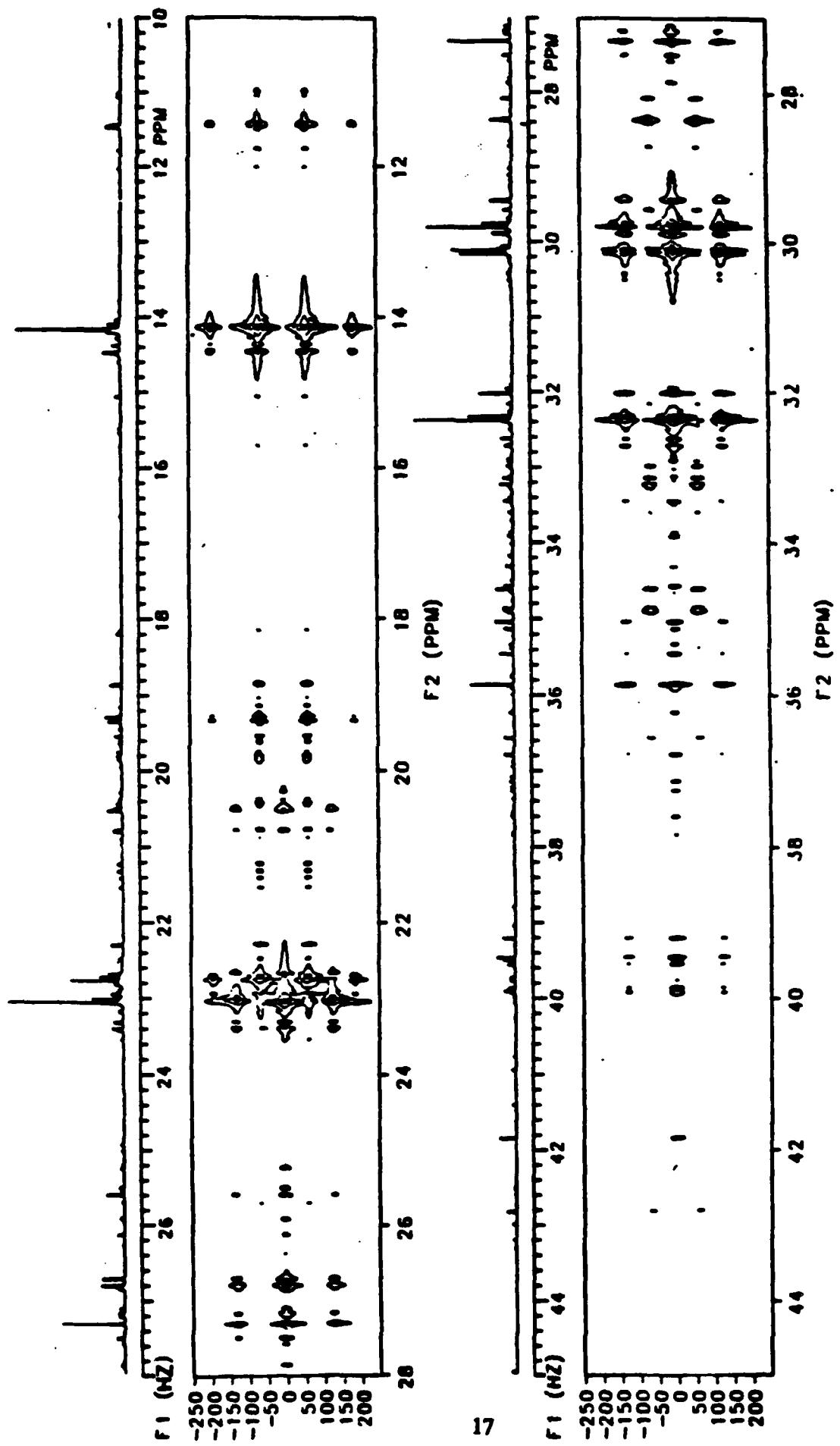


Figure 4: Contour plot of a two-dimensional proton-carbon-13 J-spectrum using the gated decoupler method on the same sample as Figure C3. The F1 axis shows proton-carbon scalar coupling; the F2 axis shows carbon chemical shifts. The proton decoupled carbon-13 spectrum is given for reference. Chemical shifts are with respect to TMS.

Table I: Summary of Carbon-Proton Correlation and J-Spectra Data for MIG-25 Fuel. Carbon intensities are relative peak heights. The number of protons attached to each carbon and their chemical shifts are indicated. Chemical shifts are relative to TMS.

Line Number	Carbon Shift	Carbon Intensity	Number of Protons	Proton Shifts
1	49.92	44.58	1	
2	43.40	43.32	1	
3	43.31	63.46	2	
4	39.76	64.45	2	0.93 1.14
5	39.67	48.35	2	1.01
6	39.64	334.07	2	1.01
7	39.33	70.26	2	1.02
8	39.06	55.39	1	
9	37.83	79.53	1	
10	37.74	55.79	2	0.96 1.14
11	37.72	48.70	2	0.96 1.14
12	37.71	55.98	2	0.96 1.14
13	37.69	63.03	2	0.96 1.14
14	37.68	48.36	2	0.96 1.14
15	37.66	91.36	2	0.96 1.14
16	37.66	79.45	2	0.96 1.14
17	37.62	204.55	2	0.96 1.14
18	37.58	76.82	2	0.96 1.14
19	37.38	55.44	2	0.96 1.14
20	37.26	65.87	2	0.93 1.14
21	37.22	75.96	2	0.95 1.13
22	36.92	45.54	2	0.95 1.13
23	36.51	59.35	2	0.84 1.50
24	35.65	51.04	2	0.65 1.50
25	35.03	43.57	2	
26	34.82	58.47	2	
27	34.67	74.52	2	
28	34.66	96.80	1	1.17
29	34.64	99.96	1	1.17
30	34.44	55.19	2	
31	34.38	42.88	2	
32	34.14	47.31	2	
33	33.70	88.45	2	0.72 1.56
34	33.69	48.19	2	0.72 1.56
35	33.65	44.03	2	
36	33.43	51.55	2	
37	33.41	56.45	2	
38	33.29	45.40	1	
39	33.28	45.67	2	
40	33.19	45.27	2	
41	33.16	77.32	2	
42	33.15	45.62	1	1.24
43	33.14	44.46	1	1.24
44	33.07	54.40	1	1.24
45	33.04	73.08	1	1.24
46	33.04	76.53	1	1.24
47	33.03	149.01	1	1.24

Table I (cont.)

Line Number	Carbon Shift	Carbon Intensity	Number of Protons	Proton Shifts
48	33.01	85.05	1	1.24
49	33.00	73.82	1	1.24
50	33.00	77.81	1	1.24
51	32.99	47.86	1	1.24
52	32.93	46.06	1	1.18
53	32.92	41.35	2	1.18
54	32.92	43.69	1	1.18
55	32.76	71.26	1	1.25
56	32.75	48.66	1	1.25
57	32.73	70.41	1	1.25
58	32.51	92.17	2	1.10
59	32.43	43.60	2	1.10
60	32.21	40.07	2	1.12
61	32.20	85.17	2	1.12
62	32.17	243.18	2	1.12
63	32.04	56.31	2	1.12
64	31.34	54.01	3	0.72
65	30.94	41.75	3	0.73
66	30.78	53.49	3	0.72
67	30.69	73.38	2	0.62
68	30.43	89.89	2	1.11
69	30.31	44.22	2	1.11
70	30.31	69.65	2	1.11
71	30.29	50.61	2	1.06
72	30.26	41.29	2	1.06
73	30.22	45.46	2	1.12
74	30.17	107.04	3	0.75
75	29.99	79.68	2	1.13
76	29.98	56.60	2	1.13
77	29.96	130.40	2	1.13
78	29.95	60.50	2	1.13
79	29.94	69.75	2	1.13
80	29.93	49.32	2	1.13
81	29.91	110.07	2	1.13
82	29.90	49.42	2	1.13
83	29.77	84.56	2	1.13
84	29.70	63.47	2	1.13
85	29.67	78.33	2	1.13
86	29.64	62.95	2	1.13
87	29.63	57.61	2	1.13
88	29.62	51.14	2	1.13
89	29.61	163.52	2	1.13
90	29.58	41.40	2	1.13
91	29.58	44.81	2	1.13
92	28.51	52.53	1	1.34
93	28.17	112.59	1	1.39
94	28.16	492.91	1	1.39
95	27.67	59.39	2	1.13
96	27.37	41.16	2	1.24
97	27.31	52.21	2	1.24

1.79

1.56

Table I (cont.)

Line Number	Carbon Shift	Carbon Intensity	Number of Protons	Proton Shifts	
98	27.26	43.82	2	1.24	1.56
99	27.25	51.71	2	1.24	1.56
100	27.13	81.13	2	1.57	
101	27.11	57.92	2	1.57	
102	27.10	56.09	2	1.57	
103	27.08	86.01	2	1.57	
104	26.98	94.69	2	1.10	1.54
105	26.97	54.02	2	1.10	1.54
106	26.96	45.30	2	1.10	1.54
107	26.95	61.67	2	1.10	1.54
108	26.94	62.56	2	1.10	1.54
109	26.93	80.41	2	1.10	1.54
110	26.89	47.34	2	1.10	1.54
111	26.87	73.66	2	1.10	1.54
112	26.85	87.19	2	1.10	1.54
113	26.83	53.09	2	1.10	1.54
114	26.65	117.75	2	1.09	1.55
115	26.64	40.41	2	1.09	1.55
116	26.62	59.72	2	1.09	1.55
117	26.61	44.32	2	1.09	1.55
118	26.61	42.58	2	1.09	1.55
119	26.50	87.29	2	1.16	1.52
120	25.52	70.07	3	0.77	
121	25.35	48.23	2	1.45	
122	25.03	256.50	2	1.08	1.09
123	24.74	63.39	2	1.14	
124	24.70	55.31	2	1.14	
125	24.70	48.67	2	1.14	
126	23.23	65.87	2	1.14	
127	23.05	42.49	3	0.71	
128	22.89	172.10	2	1.15	
129	22.88	178.61	2	1.15	
130	22.87	370.03	2	1.15	
131	22.85	73.67	2	1.15	
132	22.84	47.68	2	1.15	
133	22.82	41.33	2	1.15	
134	22.81	54.58	2	1.15	
135	22.80	47.79	3	0.72	
136	22.77	466.64	3	0.72	
137	22.75	105.62	3	0.72	
138	22.74	94.97	3	0.72	
139	22.72	238.66	3	0.72	
140	22.72	102.57	3	0.72	
141	22.70	43.37	3	0.72	
142	22.69	505.05	3	0.72	
143	22.67	52.36	3	0.72	
144	22.67	46.46	3	0.72	
145	22.65	72.06	3	0.72	
146	22.57	52.38	2	0.73	1.16
147	22.52	63.61	2	0.73	1.16

Table I (cont.)

Line Number	Carbon Shift	Carbon Intensity	Number of Protons	Proton Shifts
148	22.29	50.26	2	1.29
149	21.79	58.86	2	0.74
150	21.77	74.77	2	1.26
151	20.48	43.28	3	0.65
152	20.33	100.01	2	1.11 1.21
153	20.33	120.89	2	1.11 1.21
154	20.19	73.80	3	0.67
155	20.13	41.34	3	0.73
156	19.92	48.70	3	0.71
157	19.83	42.76	3	0.71
158	19.80	81.53	3	0.71
159	19.79	47.34	3	0.71
160	19.78	98.52	3	0.71
161	19.77	71.71	3	0.71
162	19.77	140.28	3	0.71
163	19.76	82.86	3	0.71
164	19.75	91.19	3	0.71
165	19.74	54.93	3	0.71
166	19.71	69.65	3	0.71
167	19.53	65.54	3	0.60
168	19.32	75.50	3	0.71
169	19.29	61.13	3	0.71
170	19.26	84.83	3	0.71
171	14.45	143.30	3	0.74
172	14.18	113.25	3	0.74
173	14.13	411.56	3	0.74
174	13.08	49.08	3	0.65
175	11.43	90.74	3	0.71
176	11.42	77.91	3	0.71
177	11.41	93.28	3	0.71

Table 2: Summary of Carbon-Proton Correlation and J-Spectra Data for JP-4 Fuel. Carbon intensities are relative peak heights. The number of protons attached to each carbon and their chemical shifts are indicated. Chemical shifts are relative to TMS.

Line Number	Carbon Shift	Carbon Intensity	Number of Protons	Proton Shifts	
1	44.81	65.77	2	0.53	1.62
2	42.84	61.95	1	1.36	
3	42.68	109.08	1	1.28	
4	41.70	185.42	2	1.15	
5	41.25	48.31	2	1.32	
6	40.80	53.71	1	1.18	
7	39.78	51.67	2	1.15	
8	39.76	126.78	2	1.15	
9	39.72	72.70	2	1.15	
10	39.72	65.21	2	1.15	
11	39.62	70.07	2	1.15	
12	39.58	64.50	1	0.93	
13	39.40	67.62	2	1.17	
14	39.35	135.03	2	1.17	
15	39.32	214.46	2	1.09	1.27
16	39.06	133.00	2	1.17	
17	37.00	47.09	2	1.09	1.29
18	36.94	42.97	2	1.09	1.29
19	36.65	88.26	2	1.11	1.29
20	36.42	123.15	1	1.23	
21	36.08	64.53	2	0.92	1.62
22	35.76	44.79	2	0.87	1.64
23	35.72	484.56	2	0.87	1.64
24	35.61	43.14	2	1.64	
25	35.31	178.42	2	0.77	1.63
26	35.23	46.57	1	1.91	
27	35.19	49.79	2	1.08	1.82
28	34.99	125.73	2	1.14	1.81
29	34.90	224.85	2	1.05	1.72
30	34.77	62.53	1	1.87	
31	34.76	101.96	1	1.30	
32	34.75	67.04	1	1.30	
33	34.72	129.66	1	1.30	
34	34.51	46.80	2	1.32	
35	34.47	181.02	1	1.32	
36	34.43	84.92	2	1.25	
37	34.17	99.65	2	1.16	1.73
38	34.03	55.26	1	1.39	
39	33.77	52.68	2	1.24	
40	33.72	46.27	2	0.86	1.70
41	33.45	55.74	1	2.03	
42	33.30	83.46	2	0.85	1.71
43	33.26	46.40	1	1.26	
44	33.12	44.69	1	1.26	
45	33.08	138.43	1	1.32	
46	33.00	91.69	1	1.32	
47	32.84	64.68	1	1.27	

Table 2: (Cont.)

Line Number	Carbon Shift	Carbon Intensity	Number of Protons	Proton Shifts
48	32.78	55.58	1	1.39
49	32.75	59.45	2	1.27
50	32.58	73.34	2	1.25
51	32.57	57.96	2	1.25
52	32.56	47.50	2	1.25
53	32.48	109.82	2	1.25
54	32.30	52.37	2	1.26
55	32.30	41.55	2	1.26
56	32.27	54.35	2	1.26
57	32.23	853.22	2	1.26
58	32.18	392.28	2	1.26
59	32.02	70.65	1	1.56
60	31.88	280.13	2	1.27
61	31.81	74.96	2	1.27
62	30.07	49.13	2	1.28
63	30.04	45.59	2	1.28
64	30.02	447.50	2	1.28
65	30.01	54.77	2	1.28
66	29.99	52.69	2	1.28
67	29.97	518.00	2	1.28
68	29.95	136.60	2	1.28
69	29.92	97.52	2	1.28
70	29.78	43.14	2	1.28
71	29.76	161.60	2	1.28
72	29.75	184.07	2	1.28
73	29.74	43.82	2	1.28
74	29.69	50.04	2	1.28
75	29.66	727.04	2	1.28
76	29.65	60.36	2	1.28
77	29.63	46.62	2	1.28
78	29.61	247.24	2	1.28
79	29.43	78.04	3	0.86
80	29.32	196.23	2	1.29
81	29.30	147.94	2	1.29
82	28.24	99.60	1	1.52
83	28.23	183.02	1	1.52
84	28.22	99.86	1	1.52
85	27.94	88.13	1	1.25
86	27.73	40.13	2	1.28
87	27.35	70.32	2	1.29
88	27.17	756.16	2	1.43
89	27.07	70.56	2	1.24
90	27.07	43.00	2	1.24
91	27.05	61.23	2	1.24
92	27.02	69.09	2	1.24
93	26.99	47.58	2	1.14
94	26.97	66.85	2	1.14
95	26.71	61.14	2	1.23
96	26.70	41.54	2	1.23
97	26.69	42.70	2	1.23

Table 2: (Cont.)

Line Number	Carbon Shift	Carbon Intensity	Number of Protons	Proton Shifts
98	26.68	85.74	2	1.23 1.68
99	26.66	213.36	2	1.23 1.68
100	26.65	46.00	2	1.23 1.68
101	26.57	261.52	2	1.13 1.63
102	25.99	69.30	2	1.51
103	25.78	53.43	2	1.28 1.61
104	25.46	181.14	2	1.49 1.64
105	25.41	40.50	2	1.49 1.64
106	25.36	50.43	2	1.29
107	23.29	70.02	2	1.29
108	23.26	98.61	2	1.29
109	23.18	97.58	2	1.29
110	23.03	43.25	2	1.29
111	22.91	1000.00	2	1.29
112	22.86	270.96	2	1.29
113	22.81	94.98	2	1.29
114	22.80	117.64	2	1.29
115	22.79	57.59	2	1.29
116	22.77	51.68	2	1.29
117	22.75	50.82	2	1.29
118	22.68	78.05	3	0.86
119	22.67	46.79	3	0.86
120	22.66	79.09	3	0.86
121	22.65	55.43	3	0.86
122	22.62	450.70	3	0.86
123	22.60	82.46	3	0.86
124	22.58	211.43	3	0.86
125	22.57	41.29	3	0.86
126	22.54	132.09	2	1.31
127	22.35	54.66	3	0.86
128	22.16	101.20	3	0.86
129	21.18	48.51	3	2.25
130	21.09	49.53	3	0.97
131	20.65	80.24	2	1.31
132	20.64	77.67	2	1.31
133	20.38	134.10	2	1.31
134	20.37	89.21	2	1.31
135	20.35	68.66	2	1.31
136	20.29	52.56	3	0.86
137	19.67	45.78	3	0.84
138	19.61	52.81	3	0.84
139	19.40	70.43	3	0.84
140	19.31	47.22	3	0.85
141	19.21	125.03	3	0.85
142	19.20	65.10	3	0.85
143	19.15	168.20	3	0.85
144	18.72	129.49	3	0.85
145	18.71	89.95	3	0.93
146	18.06	74.68	3	0.79
147	18.01	40.87	3	0.79

Table 2: (Cont.)

Line Number	Carbon Shift	Carbon Intensity	Number of Protons	Proton Shifts
148	14.92	74.06	3	0.88
149	14.33	76.37	3	0.88
150	14.32	142.60	3	0.88
151	14.23	75.38	3	0.88
152	14.14	44.36	3	0.88
153	14.05	116.64	3	0.88
154	14.04	101.72	3	0.88
155	14.02	916.20	3	0.88
156	13.95	107.34	3	0.88
157	13.90	43.73	3	0.88
158	11.33	114.12	3	0.86
159	11.31	118.20	3	0.86
160	11.30	82.47	3	0.86
161	11.30	75.06	3	0.86

Table 3: Summary of Carbon-Proton Correlation and J-Spectra Data for JP-5 Fuel. Carbon intensities are relative peak heights. The number of protons attached to each carbon and their chemical shifts are indicated. Chemical shifts are relative to TMS.

Line Number	Carbon Shift	Carbon Intensity	Number of Protons	Proton Shifts
1	39.82	107.60	2	1.08 1.26
2	39.76	187.13	2	1.15
3	39.45	135.97	2	1.16
4	37.84	41.24	2	1.08 1.21
5	37.73	102.27	2	1.08 1.27
6	37.72	77.11	2	1.08 1.27
7	37.50	105.11	2	1.09 1.28
8	37.48	98.51	2	1.09 1.28
9	37.46	62.38	2	1.09 1.28
10	37.44	89.37	2	1.09 1.28
11	37.38	42.48	2	1.09 1.28
12	37.16	74.64	2	1.09 1.29
13	37.04	103.84	2	1.09 1.29
14	35.14	49.37	2	0.88
15	34.79	46.16	1	1.30
16	34.78	149.21	1	1.30
17	34.55	46.04	2	0.91 1.55
18	33.81	93.67	2	0.85 1.70
19	33.16	42.32	1	1.25
20	33.14	112.12	1	1.38
21	33.12	75.17	1	1.32
22	33.03	72.00	2	1.06 1.73
23	32.87	109.87	1	1.39
24	32.63	157.83	2	1.24
25	32.41	56.76	2	1.26
26	32.32	131.14	2	1.26
27	32.30	1980.00	2	1.26
28	32.18	62.36	2	1.26
29	30.42	147.12	2	1.27
30	30.40	40.65	2	1.27
31	30.38	102.61	2	1.27
32	30.34	120.13	2	1.27
33	30.20	66.23	2	1.27
34	30.16	61.34	2	1.27
35	30.11	156.91	2	1.27
36	30.09	2020.00	2	1.27
37	30.07	121.76	2	1.27
38	30.04	1700.00	2	1.27
39	29.99	58.60	2	1.27
40	29.97	83.76	2	1.27
41	29.92	67.09	2	1.27
42	29.88	50.90	2	1.27
43	29.85	75.92	2	1.27
44	29.82	157.88	2	1.27
45	29.79	51.25	2	1.27
46	29.76	117.85	2	1.27
47	29.73	1720.00	2	1.27

Table 3: (Cont.)

Line Number	Carbon Shift	Carbon Intensity	Number of Protons	Proton Shifts
48	29.70	90.82	2	1.27
49	29.66	54.45	2	1.27
50	29.62	62.91	2	1.27
51	28.29	136.46	1	1.52
52	28.28	183.30	1	1.52
53	27.79	119.96	2	1.27
54	27.49	100.89	2	1.26
55	27.46	61.64	2	1.26
56	27.42	40.20	2	1.26
57	27.11	125.24	2	1.26
58	27.09	95.91	2	1.26
59	27.04	55.51	2	1.14 1.63
60	26.77	116.53	2	1.22 1.68
61	26.73	44.93	2	1.22 1.68
62	25.45	61.64	2	1.55
63	25.15	124.83	2	1.29
64	23.34	116.58	2	1.27
65	23.10	68.05	3	1.29
66	23.00	226.00	2	1.29
67	22.99	1860.00	2	1.29
68	22.90	45.05	3	0.87
69	22.87	73.02	3	0.87
70	22.83	220.22	3	0.87
71	22.79	49.16	3	0.87
72	22.78	353.32	3	0.87
73	22.74	225.25	3	0.87
74	22.71	43.57	3	0.87
75	20.44	54.33	2	2.18
76	20.44	160.04	2	1.30
77	19.84	65.04	3	0.84
78	19.84	65.65	3	0.84
79	19.83	131.69	3	0.84
80	19.82	48.08	3	0.84
81	19.80	75.01	3	0.84
82	19.37	42.11	3	0.84 1.27
83	19.34	144.48	3	0.84 1.27
84	19.32	48.07	3	0.84 1.27
85	14.50	139.88	3	0.87
86	14.30	51.90	3	0.87
87	14.23	124.96	3	0.87
88	14.19	1580.00	3	0.87
89	14.07	58.91	3	0.87
90	11.49	41.53	3	0.85
91	11.47	108.57	3	0.85

a lot has been learned about just how to take the data for best results on these samples. Due to time constraints the other samples could not be repeated. There are many ambiguities in Table 4 because of the fact that there are many compounds of similar structure and, hence, similar chemical shifts in the sample. Although the individual resonances can be resolved in the one-dimensional spectrum, because of the data system limitations mentioned earlier the two-dimensional spectra do not have as good resolution. Nevertheless, it is possible to learn much about the nature of the sample as Figure 7 illustrates. The unsatisfied bonds in the fragments occur at points where the structures of the various compounds diverge sufficiently to make the connectivities unobservable. Several of the fragments have carbons in common indicating that the molecules in question have parts that are similar and parts that are not. Our understanding of this data is, as yet, incomplete. It would be desirable to run more model compounds and known mixtures to learn how they behave.

Each fragment is characterized by chemical shifts for each atom, C-H and C-C coupling constants, C-H bonds, and C-C bonds. There currently exist both proprietary and public domain data bases which contain carbon chemical shift data. Various search techniques are available. Data bases can be searched by chemical shift lists, by compound name and by compound formula. Simulations of 1-D spectra can be performed as well. Searches for possible compounds containing a fragment can be done. All of the above data are not contained in them, and they are not organized conveniently for searching for simultaneous matches to both carbon and proton data. Creating new databases is beyond the scope of this project, but perhaps one could at least develop better ways to organize and search the existing databases which would take some advantage of the correlations available from the 2D NMR data.

As a first step in the automation of the analysis of the types of data discussed above we are currently engaged in development of software to assist in the analysis of phase-sensitive 2-D INADEQUATE spectra which will be discussed below in Section F.

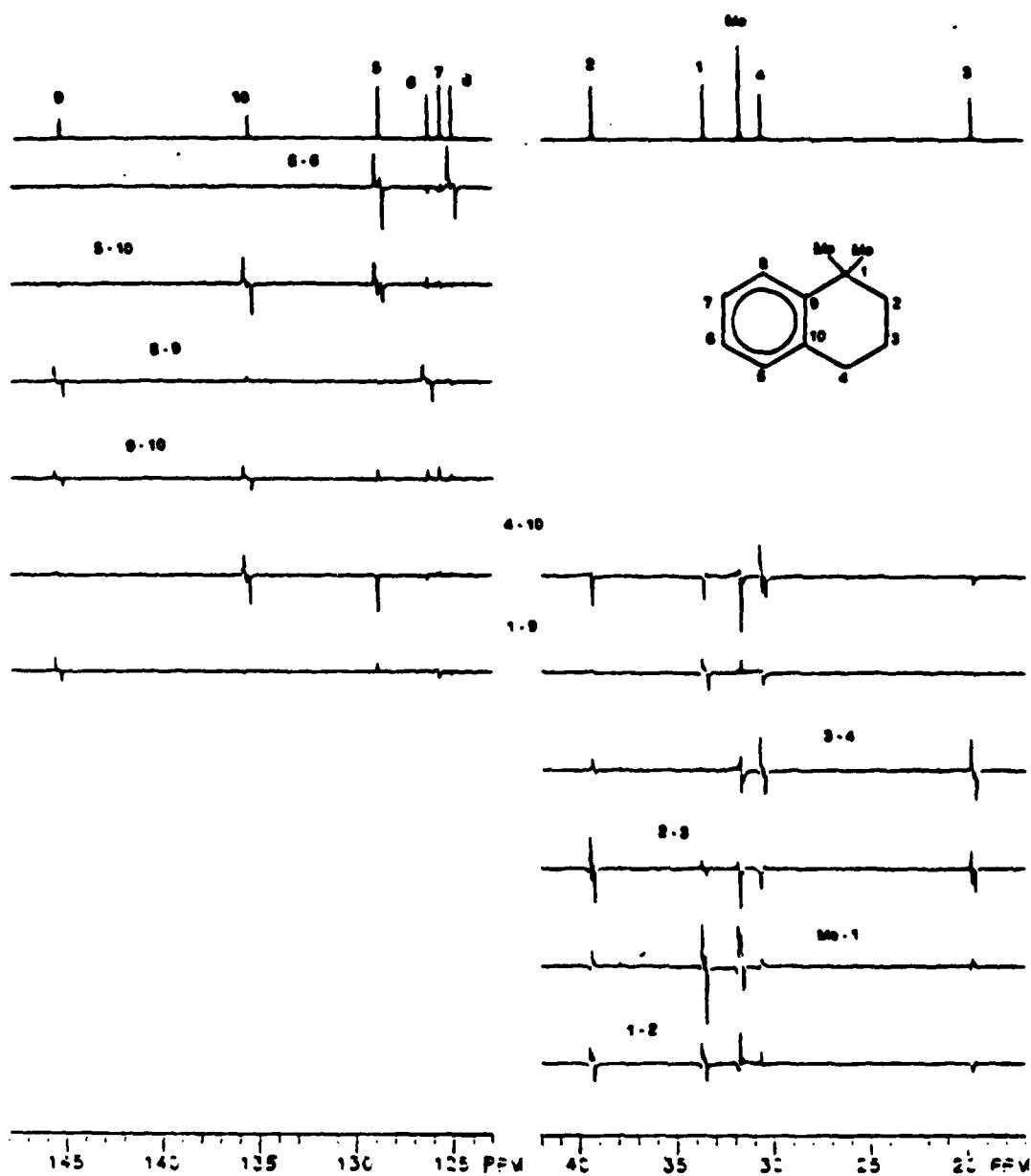


Figure 5: Two dimensional INADEQUATE spectrum of 1,1-dimethyltetralin 60% in deuteriochloroform. The proton decoupled carbon spectrum at the top is assigned with reference to the inset structure. Each trace is taken from the data set at the F1 frequency corresponding to the double quantum frequency of the pair of bonded carbons as labelled. Each trace exhibits clearly an AX four line pattern corresponding to the appropriate bond. (See figure D2.) The extraneous signals in each trace result from imperfect suppression of the two hundredfold more intense single quantum resonances. The 6-7 and 7-8 bonds are not shown because they are close enough together to be AB rather than AX in nature and do not produce clean four line patterns. Chemical shifts are with respect to TMS.

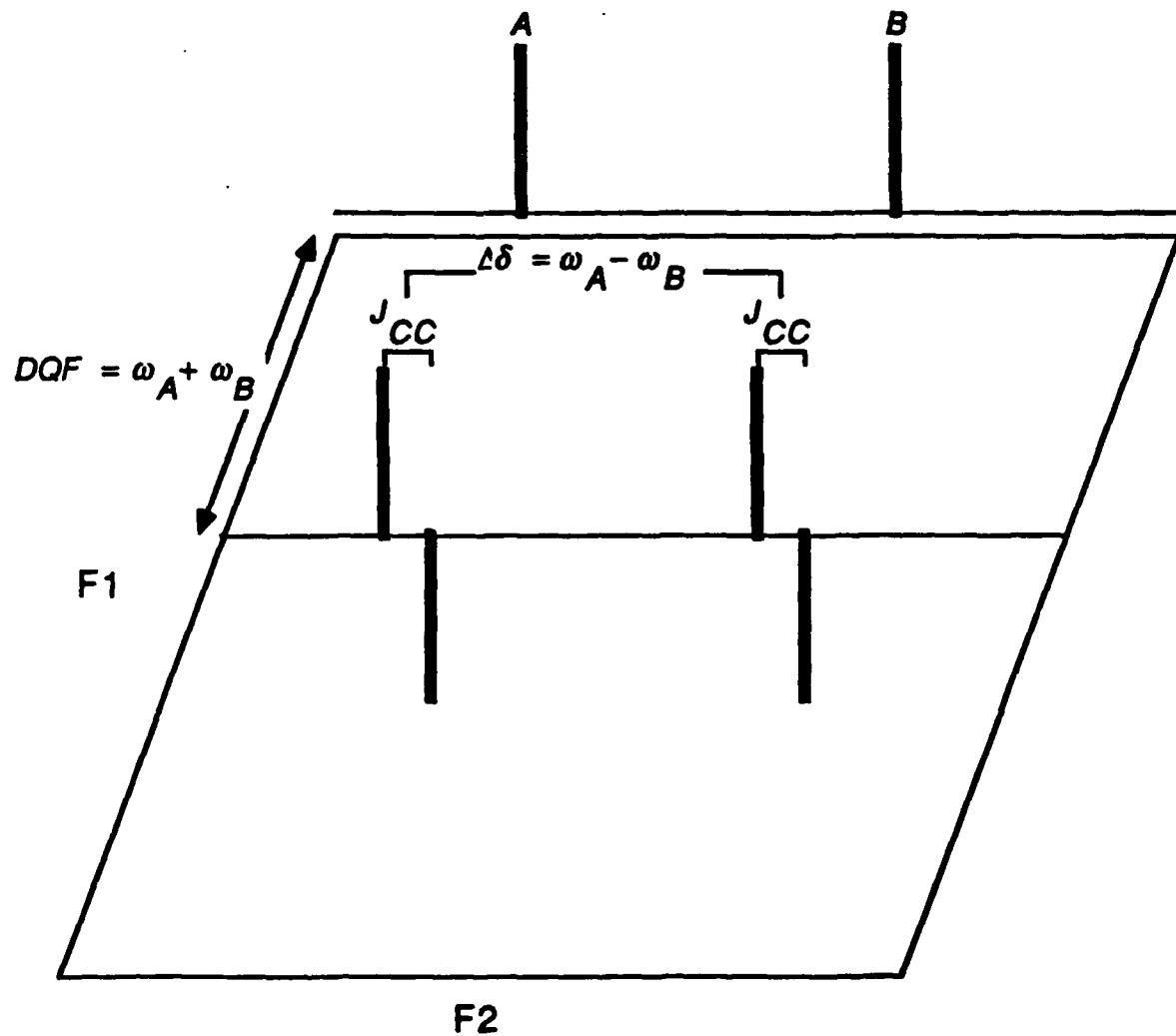


Figure 6: Schematic diagram showing how each pair of bonded carbons produces a characteristic four line AX pattern displaced along F1 by the double quantum frequency (DQF). Note that the chemical shifts and DQF may be perturbed by a few hertz with respect to the resonances in the ordinary carbon spectrum due to isotope shifts of a molecule with two carbon-13's compared to one with only one.

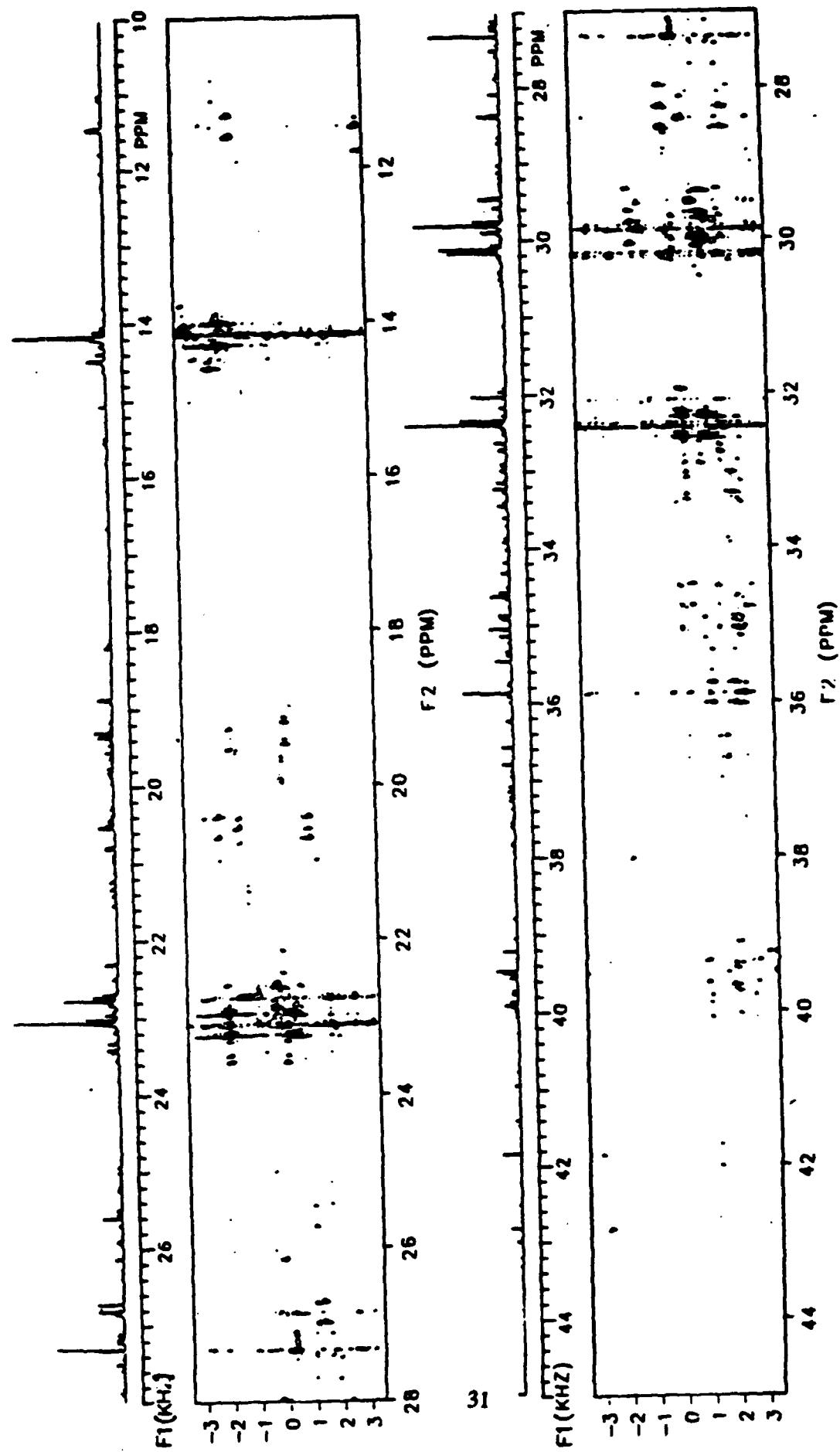


Figure 7: Contour map of a 2D INADEQUATE spectrum of JP-4 (same sample as previous figures). The proton decoupled carbon spectrum is given for reference. Chemical shifts are with respect to TMS. The data set is phase sensitive although the negative contours are not differentiated in a black and white presentation. Even though the spectrum is quite complex, characteristic doublet patterns can be seen for many of the resonances.

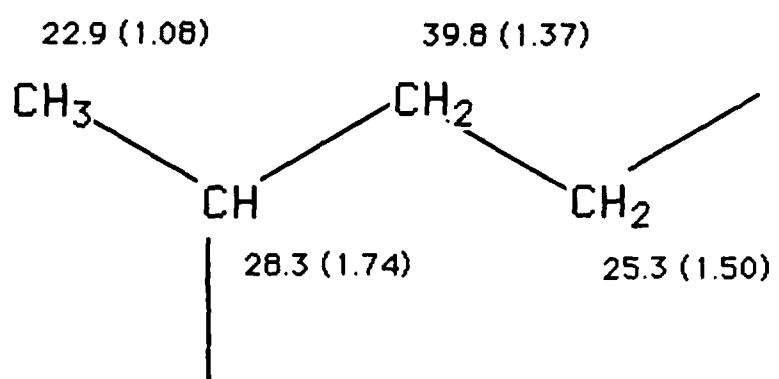
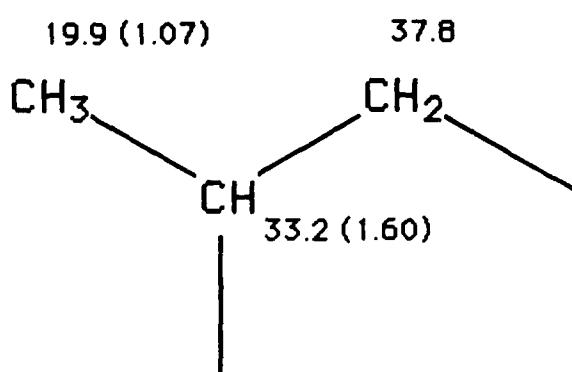
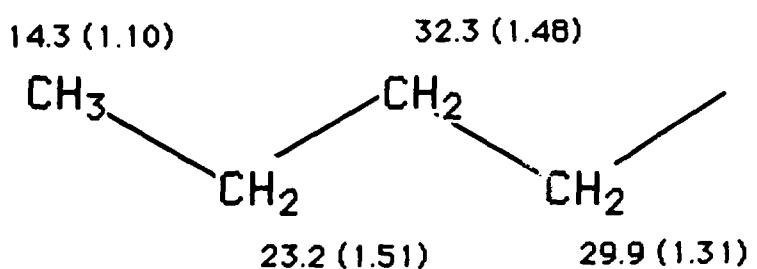


Figure 8: Molecular fragments extracted from the various spectral data for MIG-25 fuel. Numbers are carbon chemical shifts with proton chemical shifts in parentheses. Shifts are with respect to TMS.

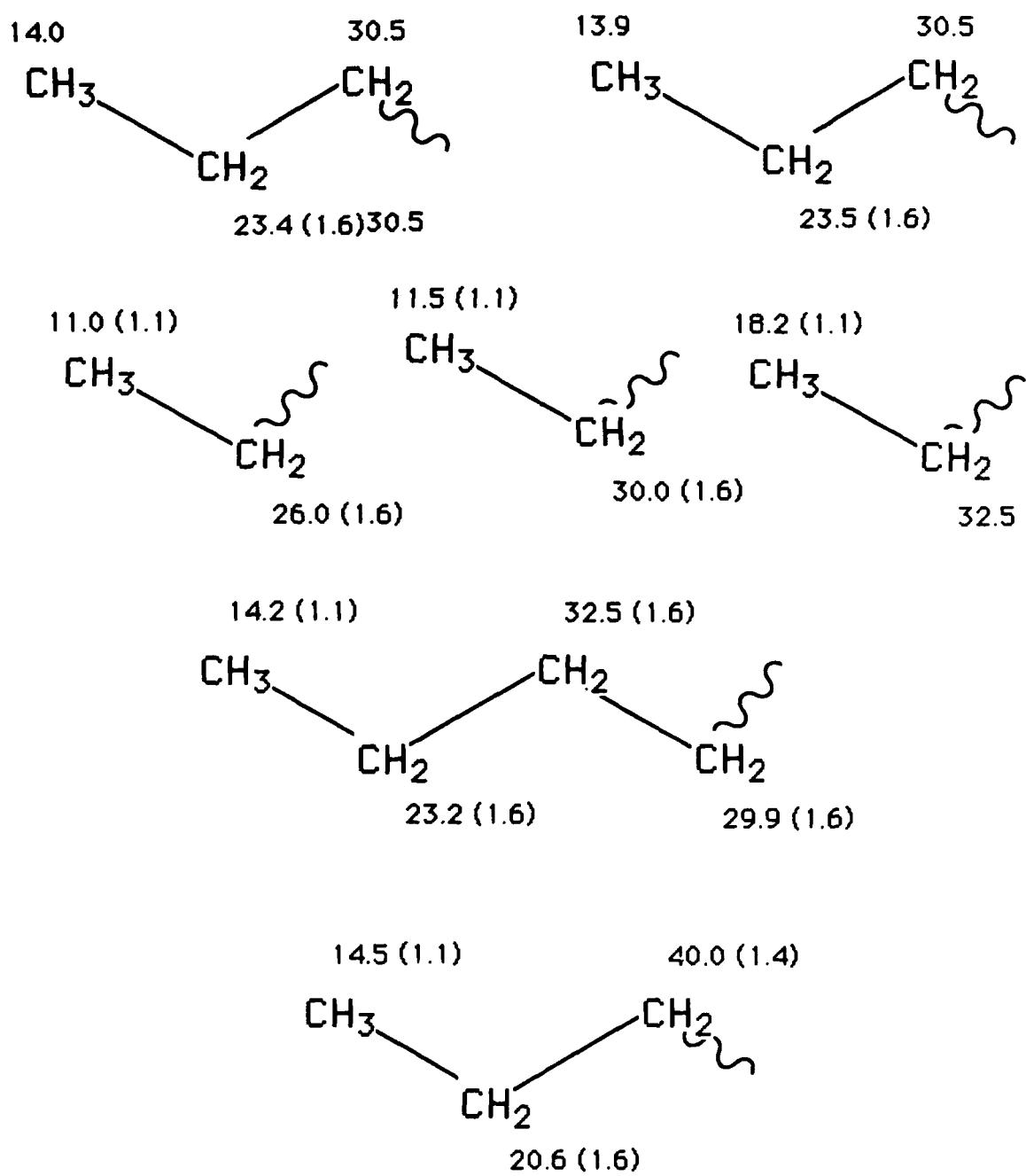


Figure 9: Molecular fragments extracted from the various spectral data for JP-4 fuel. Numbers are carbon chemical shifts with proton chemical shifts in parentheses. Shifts are with respect to TMS.

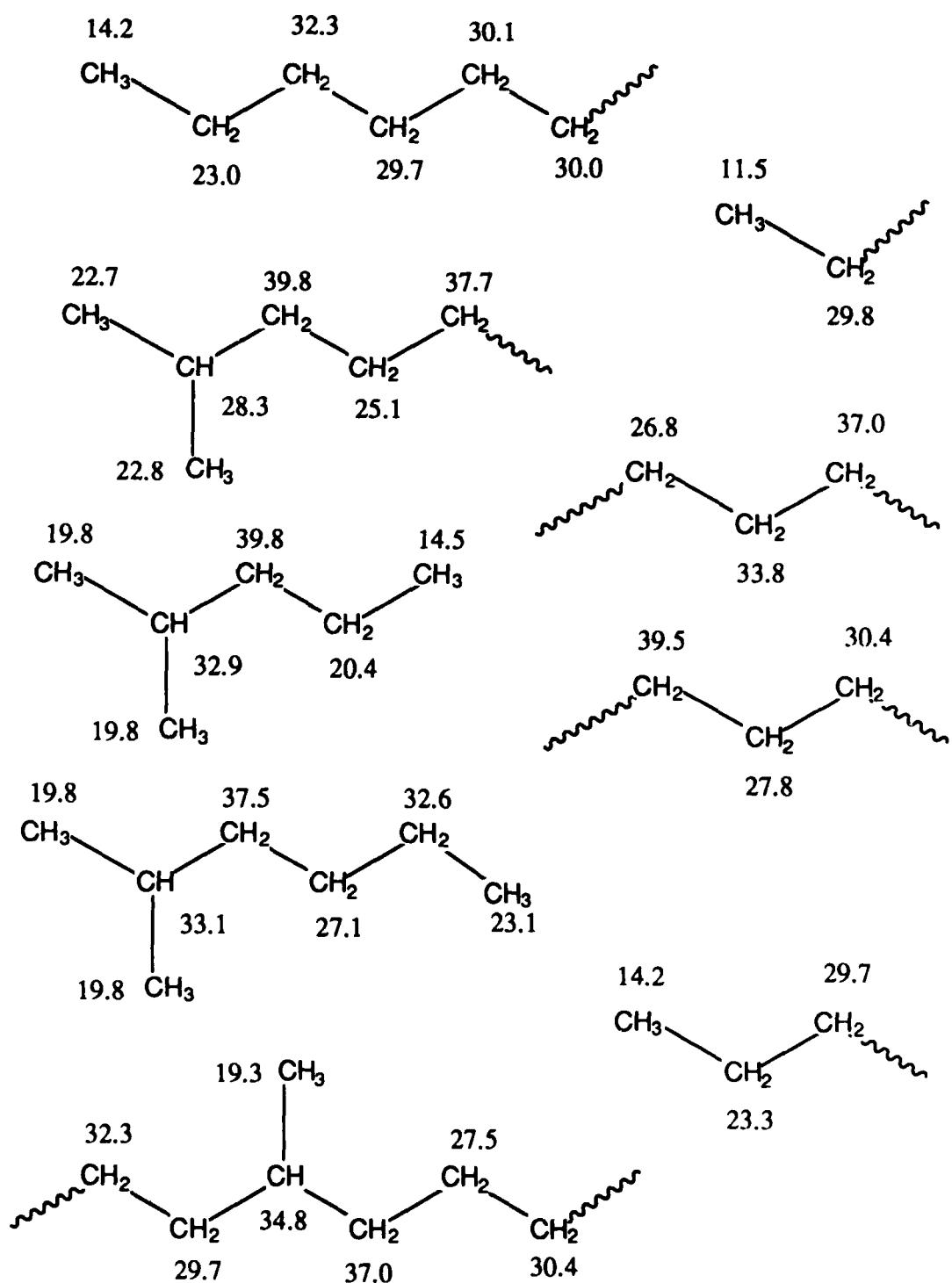


Figure 10: Molecular fragments extracted from the various spectral data for JP-5 fuel. Numbers are carbon chemical shifts. Shifts are with respect to TMS.

Table 4: List of Connectivities for JP-5 Fuel. Line numbers refer to similar numbers in Table C-III where proton shifts for each line can be found.

Fragment Number	Carbon 1 Chemical Shift	Carbon 1 Line Number	Carbon 2 Chemical Shift	Carbon 2 Line Number	Carbon 1 J_{CC}	Carbon 2 J_{CC}
1	29.67	47	30.09	38	35.2	33.9
1	29.72	47	32.30	27	34.7	34.7
1	22.98	67	32.29	27	34.2	34.6
1	14.17	88	22.98	66	34.7	35.1
2	22.74	73	28.28	51;52	34.8	34.9
2	22.77	72	28.28	51;52	34.8	34.9
2	22.82	70	28.28	51;52	35.2	34.9
2	28.27	51;52	39.45	3	34.7	34.4
2	28.27	51;52	39.76	2	34.7	34.2
2	25.14	63	39.76	2	35.3	34.2
2	25.14	63	37.73	5;6	35.2	34.1
3	14.49	85	20.44	76	34.7	34.4
3	20.43	76	39.82	38	35.1	34.8
3	32.87	23	39.82	38	35.3	35.6
3	19.83	79	32.88	23	35.4	35.3
3	19.80	81	32.88	23	34.8	35.3
4	27.10	57	32.63	24	34.3	34.9
4	23.10	65	32.63	24	35.3	34.7
4	27.10	57	37.45	10	34.7	34.6
4	27.10	57	37.50	7	34.7	34.4
4	33.13	19;20;21	37.47	7;8;9;10	35.3	35.3
4	19.82	77;78;80	33.13	19;20;21	35.6	35.9
5	29.72	48	34.78	16	34.4	34.8
5	19.34	83	34.77	16	34.9	35.8
5	34.77	16	37.05	13	35.4	34.4
5	32.30	26	29.71	48	34.3	34.3
5	27.49	54	37.04	13	34.8	34.7
5	27.46	54	30.34	32	34.7	35.2
5	27.46	54	30.38	31	34.7	34.3
5	27.46	54	30.43	29	34.7	34.8
5	14.21	87	23.33	64	34.8	34.4
5	23.33	64	29.70	48	34.2	34.6
5	27.78	53	39.45	3	34.2	34.3
5	27.78	53	0.00		34.9	0.0
5	26.76	60	33.82	18	33.2	32.8
5	33.81	18	37.05	13	33.4	34.4
6	11.46	91	29.82	44	35.4	34.7

E. ^2H Spectroscopy

Deuterium has long been used in nuclear magnetic resonance studies as a kinetic, mechanistic, and structural probe.^{8,9,10,11,12,13} Most work has involved enrichment as a result of the ready availability and relative ease of isotopic incorporation. It is only recently that ^2H NMR studies at natural abundance have become feasible as a consequence of Fourier transform methods, which make signal averaging possible on a short time scale, and very high field spectrometers, which are necessary for sufficient resolution to separate closely placed resonances resulting from the low magnetogyric ratio of ^2H (ratio of $^1\text{H}/^2\text{H}$ magnetogyric ratios is 0.1535).

As with other rare nuclei such as ^{13}C and ^{15}N , proton-decoupled natural abundance deuterium NMR spectra exhibit single resonances for each chemically distinct site. Deuterium relaxation is dominated by the quadrupolar mechanism with short T_1 values, assisting in the accumulation of data. NOE contributions to line intensities are negligible due to the unimportance of the dipolar relaxation process, so no special care need be taken to obtain a spectrum with quantitative intensities.

Deuterium has been used very frequently in the past as a probe into reaction pathways and mechanisms through $^1\text{H}/^2\text{H}$ kinetic isotope effect (KIE) studies. Enrichment of deuterium has been necessary. The two most common methods of studying such effects are by comparison of absolute reaction rates of the enriched and unenriched compounds or by intermolecular competition between the two. Relative amounts of enriched and unenriched compounds in the latter case have been measured by mass spectroscopy. The use of enrichment has several drawbacks. It can be extremely difficult to perform site-specific enrichments in a particular compound. Measurement of KIE's are complicated by a combination of primary and secondary effects when a compound has equivalent hydrogenic sites. Site-specific data are not available from mass spectroscopic sources, since substantial scrambling of protons occurs in the parent molecular ion.¹⁴

Anomalous intensity patterns which arise from $^1\text{H}/^2\text{H}$ KIE's have been observed in high-field, proton-decoupled, natural abundance deuterium NMR spectra.^{14,15,16,17,18,19} These anomalies provide a unique and powerful tool for the investigation of reaction mechanisms through

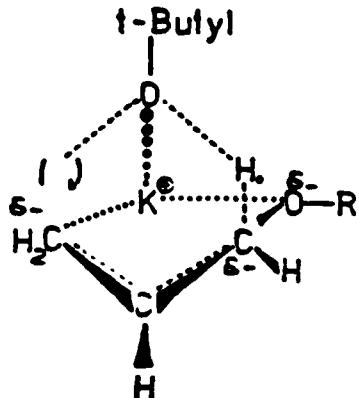
$^1\text{H}/^2\text{H}$ KIE's. The complications associated with enriched compounds are removed and site-specific data related to the reaction history of compounds are available. Observation of ratios of integrated peak intensities in the natural abundance ^2H spectra can provide valuable insight into reaction mechanisms.

One such investigation into the base-catalyzed rearrangement of allyl phenyl ether to propenyl phenyl ether produced new data which required a re-assessment of the accepted mechanism for rearrangement. This rearrangement has been represented as a true, three-carbon prototropic shift.^{20,21} The product of the rearrangement is 97-99% *cis*.

Price and Snyder²⁰ have proposed a mechanism to explain the overwhelming stereospecificity of the reaction. They suggested that the hydrogen alpha to the etheric oxygen (see Figure 11) is stabilized by attraction to the *tert*-butoxide oxygen and that the carbanionic intermediate is stabilized by the cation of the base. They further proposed that this proton then migrates to the terminal carbon forming a methyl group at which time the reaction is complete and the intermediate complex separates.

As this rearrangement involves both C-H bond cleavage and formation it becomes an ideal candidate for study by natural abundance ^2H NMR. Figure 12 contains the natural abundance spectra of the allyl and propenyl ethers. In the Price mechanism, the site beta to the ether oxygen will not participate in the reaction. The uninvolved phenyl group is used as an internal concentration reference and set arbitrarily to a value of 5.

Figure 11. Schematic of Price and Snyder's reaction mechanism for the rearrangement of allyl to propenyl ethers. The hydrogen alpha to the oxygen is labeled by the oxygen of *tert*-butoxide. The allylic anion is stabilized by the counter ion to the base. An intramolecular hydrogen transfer occurs from alpha to gamma.



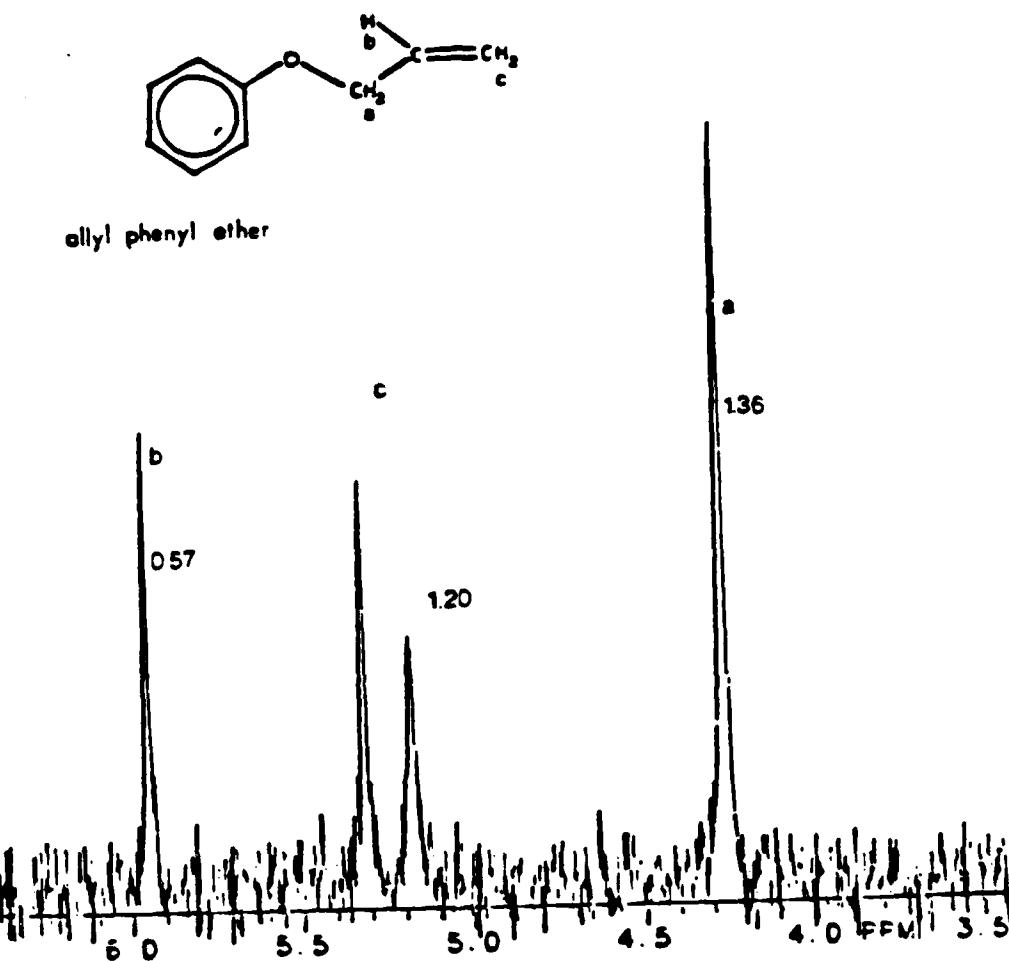
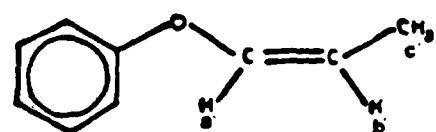


Figure 12. Natural abundance spectra of a) allyl and b) propenyl phenyl ethers. The phenyl group (not shown) serves as internal concentration reference with an arbitrary intensity of 5.00. In the allyl ether the hydrogen at b (5.95 ppm) has a relative concentration of 0.57, the terminal methylene exhibits two peaks which are summed to 1.20 relative and the methylene adjacent to the oxygen has a relative concentration of 1.36. In the propenyl ether the b' site at 5.29 ppm has a relative concentration of 0.47, peak a' (6.74 ppm) has a relative concentration of 0.63, and the methyl group, c' (2.17 ppm) has a relative concentration of 1.26. There has been a loss of 0.73 from the a site which has not been gained by the c site. There has also been a loss of 0.14 going from b to b'.

b



propenyl phenyl ether

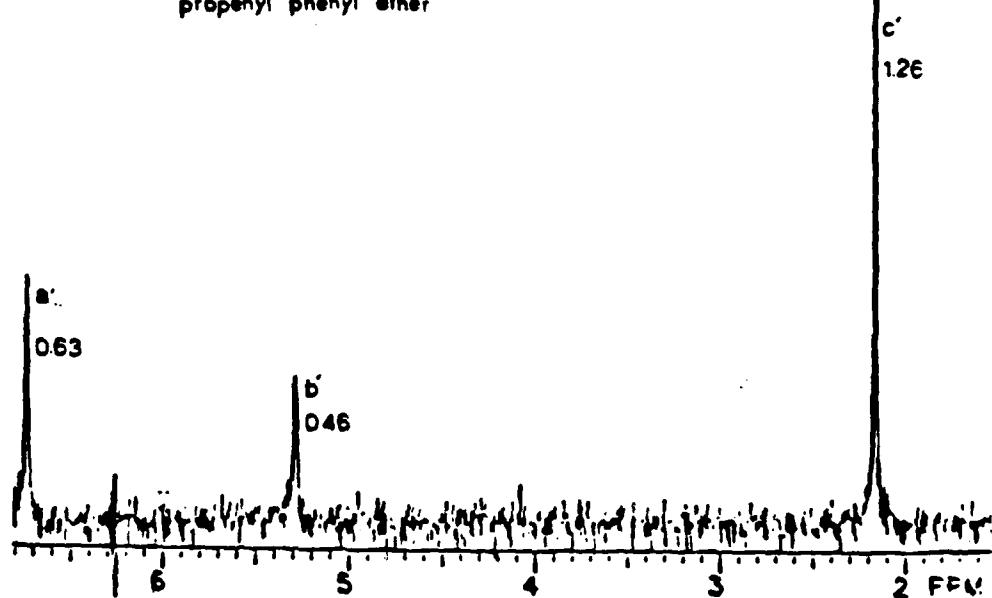


Figure 12 b) propenyl phenyl ether. See Figure 12 a for details.

The Price mechanism would require that all of the deuterium lost from the alpha position in the allyl ether be transferred in a concerted manner to the terminal carbon. A comparison of the two spectra demonstrates that this is not the case. The depletion in deuterium concentration at the methyl site of propenyl ether relative to the expected value requires that there be another source of hydrogen for C-H bond formation. Surprisingly, the beta peak, which was expected to be unaffected, also exhibited a loss of deuterium concentration in going from the allyl to propenyl ether. There is no explanation in the concerted mechanism for such a loss.

Prosser²¹ and Broaddus²² found results indicating that an intermolecular transfer was at least a possible competing mechanism. Price's mechanism was performed for work performed in DMSO with *tert*-butoxide present in catalytic quantities. DMSO has been shown to enhance the catalytic effects of the base. We examined a solution of 0.05M potassium *tert*-butoxide in DMSO by NMR and demonstrated that the acid/base equilibrium lies substantially to the side with *tert*-butanol and $\text{CH}_3\text{CH}_2\text{SO}^-$. This is important to the postulation of a two-step mechanism, since otherwise the amount of ether reacted would be limited by the initial concentration of *tert*-butoxide. However, it appears that the anion of DMSO acts as the base and is regenerated from the solvent as the etheric anion is protonated.²³

The results of the ^2H NMR studies indicated that a two-step mechanism must be proposed for the rearrangement, and that the new proposed mechanism must account for reactivity in the beta site as well as in the alpha and methyl sites. This site-specific data has been available from no other studies.

F. Data Base and Pattern Recognition Work

The analysis of complex mixtures, such as fuels, requires the solution of problems distinct from the analysis of pure compounds. It is necessary to separate out components of the mixtures and to then identify those components. The identification problem of components can draw on work which has been done in the identification of pure compounds. Comparison of spectra of unknown compounds to libraries of spectra of known compounds has begun to be automated in spectral data bases. We acquired the EPA/NIH ^{13}C data base from Professor C.L. Wilkins at the

University of California at Riverside. This data base was transferred successfully to our VAX 11/750 and routines were completed that allowed reading and writing to the data base. For our purposes, only the hydrocarbon entries were extracted (approximately 1000 compounds) and used for searching. We have been successful in using the reduced data base to perform searches for possible compounds containing specific fragments.

The obtaining of the fragments or components present in a complex mixture is a different problem. We have approached this problem with the technique of the 2-D INADEQUATE NMR experiment. The 2-D INADEQUATE experiment yields information about C-C connectivities and allows the spectroscopist to build a structural skeleton. Unfortunately the experiment suffers from poor sensitivity and the necessity for long acquisition times. It is also difficult for the spectroscopist to analyze the resulting 2-D contour plot. We have worked on developing computer software to automate the analysis of these spectra. The goals of this software are to speed the analysis of the spectra and to improve the amount of data which can be extracted from noisy spectra.

To develop an automated system for pattern recognition for ^{13}C connectivities as detected by the 2-D INADEQUATE NMR experiment, it is necessary to devise an algorithm that will identify the features of a spectrum which contain the connectivity data. The connectivities are contained in the characteristic AX patterns (see Figure 13) consisting of pairs of plus-minus doublets in the 2-D plot which have equal double quantum frequency (DQF), by the chemical shifts of the two bonded carbons, and by the one-bond scalar coupling constant ($^1\text{J}_{\text{CC}}$) for the two carbon atoms. In principle, any pair of lines from the line list of a proton-decoupled 1-D carbon spectrum could represent a bond. DEPT or 2-D J-spectral data can be used to limit the number of possible C-C bonds for each carbon resonance based on the number of protons attached to each carbon. Also, the intensities of the lines must be commensurate. Our experience has been that the antiphase doublets of the phase sensitive experiment are more easily recognized in low signal to noise situations and the computer algorithm takes advantage of this additional information.

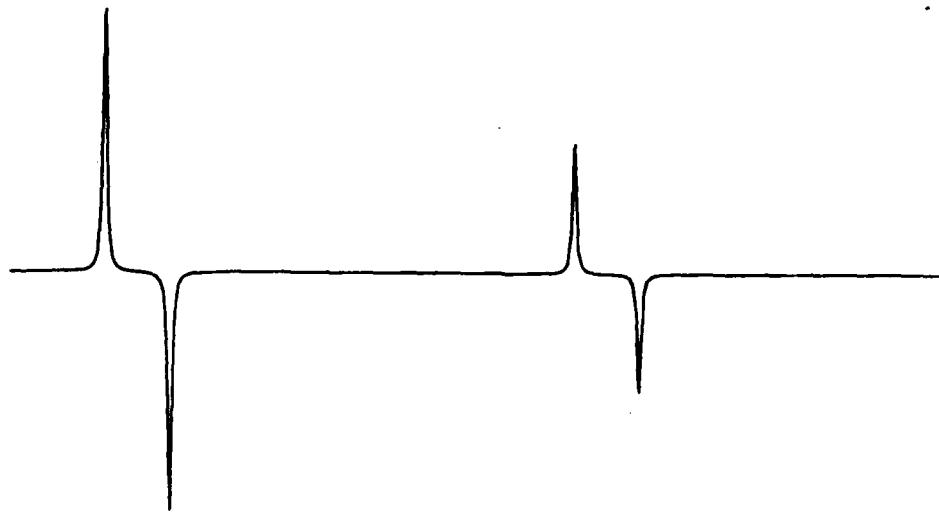


Figure 13. Simulation of a two-carbon, one-bond system showing how each pair of bonded carbons produces a characteristic four line AX pattern displaced along F1 by the double quantum frequency (DQF). This is a trace at the DQF demonstrating the plus-minus characteristics of the doublets seen in the phase-sensitive experiment. The differences in intensities in the pairs of doublets arises from the use of different degeneracy values in the simulation. Note that in a real spectrum the chemical shifts and DQF may be perturbed by a few hertz with respect to the resonances in the ordinary carbon spectrum due to isotope shifts of a molecule with two ^{13}C 's compared to one with only one.

To have a well-controlled data set with which to test the pattern-recognition software, a package to simulate 2-D INADEQUATE spectra was written. The simulation routines accept chemical shifts, intensities, coupling constants and relaxation parameters as inputs and generate a simulated 2-D spectrum with Lorentzian lineshape functions. The equation used for the simulation and matching in the frequency domain is given below. Pseudo-random noise is generated and added to the simulated spectrum to more closely emulate a real spectrum.

The pattern matching routines require input of a line list from a quantitative 1-D ^{13}C spectrum and a properly phased 2-D INADEQUATE spectrum. The chemical shifts from the 1-D spectrum are sorted by intensity and pairs with reasonable intensity ratios are selected. The double quantum frequency is calculated from the chemical shifts. A subset of the 2-D data array

consisting of two rectangles centered on the two points defined by the chemical shifts and ν_{DQ} and large enough to encompass any reasonable values of the coupling constant is searched for signals matching the four line antiphase pattern. We currently use a simplex routine to perform non-linear surface fitting with seven adjustable parameters: the intensities of the two doublets, I_A and I_B ; the one-bond scalar coupling constant, J ; the two chemical shifts, ν_A and ν_B ; the double quantum frequency, ν_{DQ} ; and a relaxation time to adjust the line width in each dimension, T_{2DQ} and T_2 . with

$$\nu_{DQ} = \nu_A + \nu_B.$$

The equation for the theoretical pattern to be searched for is

$$S(\nu_1, \nu_2) = \frac{1}{1 + (\nu_1 - \nu_{DQ})^2 T_{2DQ}^2} \left[I_A \left(\frac{1}{1 + \left(\nu_2 - \nu_A + \frac{J}{2} \right)^2 T_2^2} - \frac{1}{1 + \left(\nu_2 - \nu_A - \frac{J}{2} \right)^2 T_2^2} \right) + I_B \left(\frac{1}{1 + \left(\nu_2 - \nu_B + \frac{J}{2} \right)^2 T_2^2} - \frac{1}{1 + \left(\nu_2 - \nu_B - \frac{J}{2} \right)^2 T_2^2} \right) \right]$$

Of course, the same equation is used in the simulation software to generate the test data sets. See Figure 14 for a schematic representation of the program. We have used output from the simulation package to begin testing the pattern matching software. The simulated spectrum with pseudo-random noise is used as input by the pattern-matching software which predicts the spectral parameters using the rms difference between the prediction and the simulated spectral data. Table 5 and Figure 15 exhibit the values recovered for spectra containing varying amounts of noise. Even with a peak-to-peak noise level of 100% of the amplitude of the largest peak, the recovered values agree remarkably well with the values used in creating the simulation.

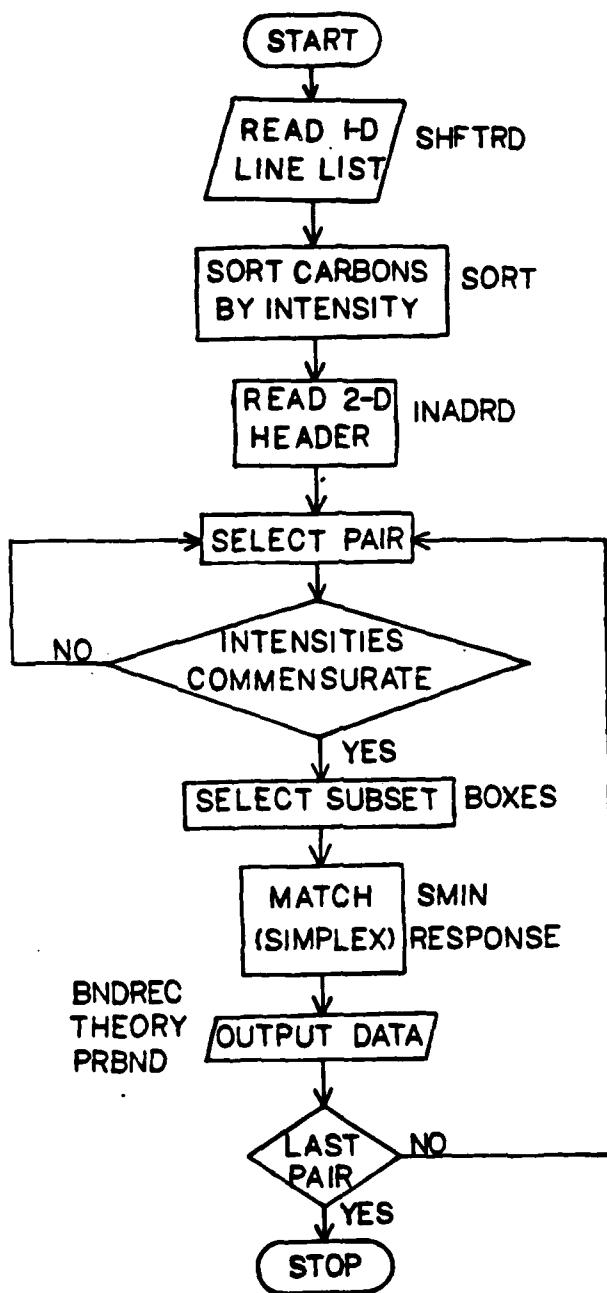


Figure 14. Top-level flowchart of the pattern-matching program. Subroutines which accomplish each task are listed outside the boxes. The software is still experimental. It would be desirable to incorporate criteria for determining whether or not there is a bond present from the results of the surface fitting. It is currently necessary to analyze the output of the program personally. Even so, it occupies much less of a spectroscopist's time to analyze the output data than to analyze an entire 2-D spectrum.

Table 5. Results of Pattern Matching on Simulated Spectra with Pseudo-Random Noise^a

Parameter	0%	10%	20%	50%	75%	100%	200%
I ₁ ^b	1.000	1.059	1.088	1.116	1.002	1.000	1.004
I ₂	2.000	1.852	931	2.163	2.234	2.344	2.435
1J _{CC}	35.00	34.78	34.57	35.88	35.95	34.65	34.80
Shift ₁ ^c	1180.0	1180.1	1180.1	1179.2	1179.2	1180.2	1180.2
Shift ₂	1430.0	1429.8	1429.7	1429.7	1429.7	1429.6	1429.4
T2 ^d	1.000	1.063	1.298	1.030	1.178	1.085	1.037
TDQ	1.000	1.011	0.944	1.014	0.938	0.998	0.998

a) Noise percentage is given as percentage of the absolute value of the maximum or minimum of the largest peak in the 2-D spectrum. The table entries under 200%, therefore, represent a spectrum with noise generated which is 100% of the peak-to-peak magnitude of the largest doublet in the spectrum.
 b) The relative intensity factor for carbon 1.
 c) Chemical shift for carbon 1.
 d) T2 and TDQ are line width parameters in the chemical shift and double quantum frequency dimensions.

The parameters used in simulating the target spectra are exactly as found in the 0% noise column.

We have also made a simulation of 1,1-dimethyltetralin and recovered the appropriate parameters satisfactorily using the pattern-matching software. We are using data from a real spectrum of 1,1-dimethyltetralin as a model compound for testing the software on real data.

Experimental 2-D INADEQUATE spectra exhibit extraneous signals which arise from incomplete suppression of the two-hundredfold more intense singly-substituted molecules. The pattern-matching software attempts to avoid finding the extraneous signals by placing constraints on the coupling constant and on the chemical shifts. It is well known that C-C coupling constants are limited to the range 30 to 60 Hz. Further limitations relating to the hybridization of the carbons are also known. The software currently uses the overall range as a general constraint, but it is intended that the penalty function will be extended to set limits depending on the chemical shifts of the two carbons being investigated. The chemical shifts in the 2-D spectrum may not match exactly those in the 1-D experiment due to small isotope shifts caused by double substitution. The amount

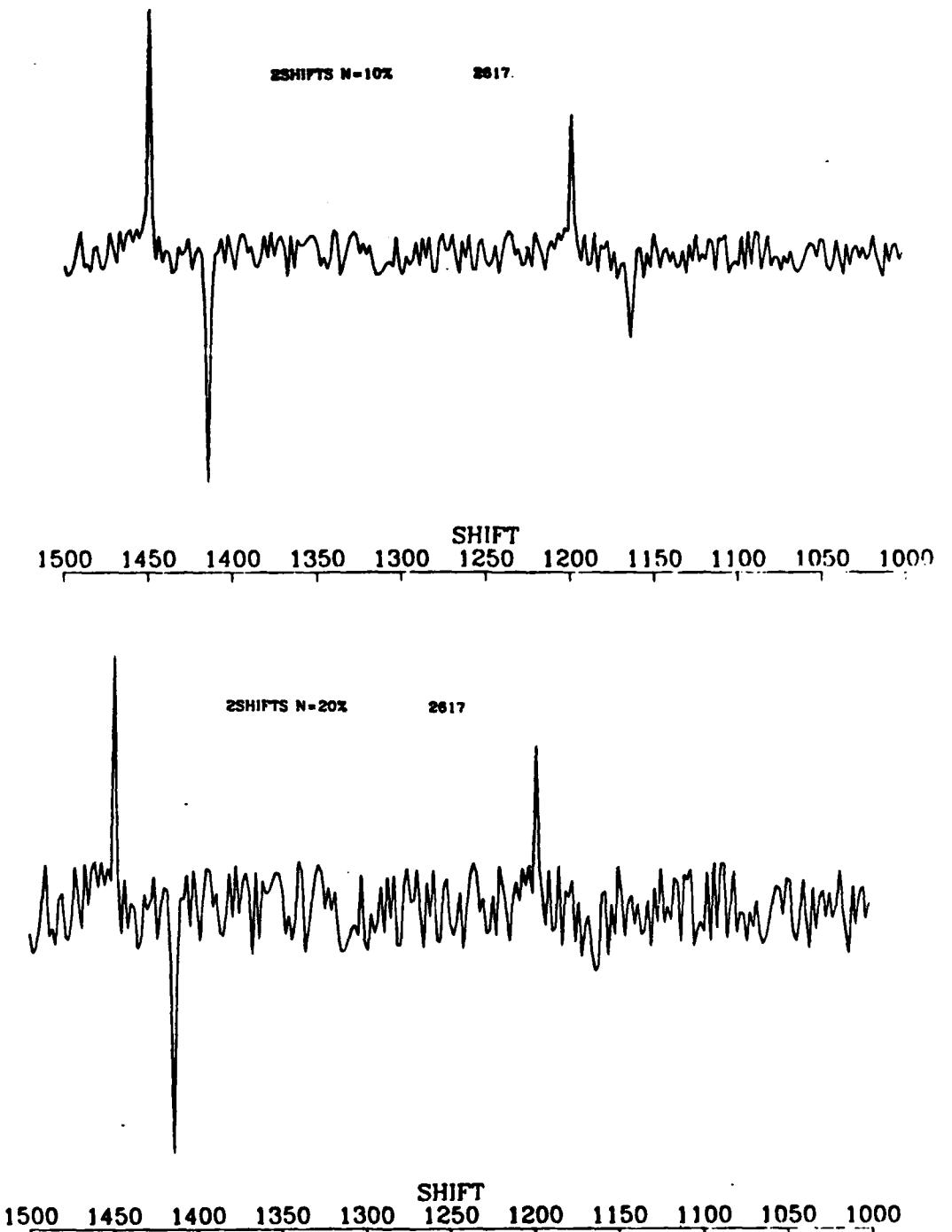


Figure 15. a) Noise level 10 and 20 percent. Simulated spectra (same simulation parameters as Figure 13) showing increasing amounts of pseudo-random noise. The noise level is as a percent of the absolute value of the largest positive or negative peak in the 2-D spectrum. The spectrum labelled 200%, therefore, has noise added of the same magnitude as the peak-to-peak measurement of the largest peaks in the theoretical spectrum. In order to fit the last spectrum on the page, it was necessary to reduce the vertical scale by a factor of 2 with respect to the other spectra.

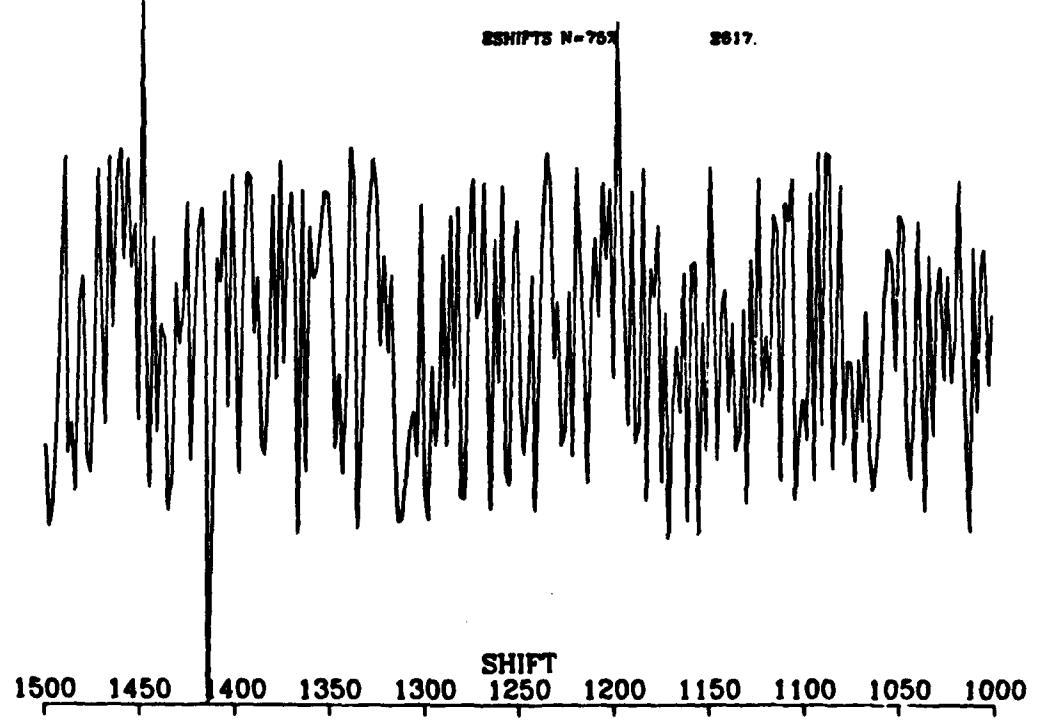
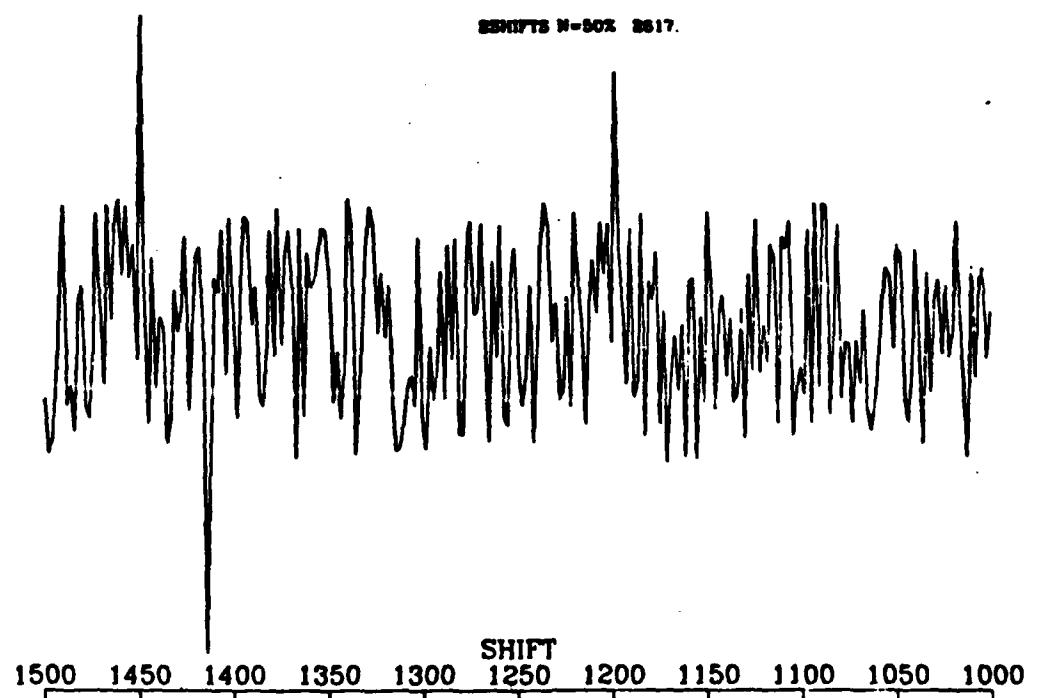


Figure 15. b) Noise level 50 and 75 percent. See Figure 15 a for detailed caption.

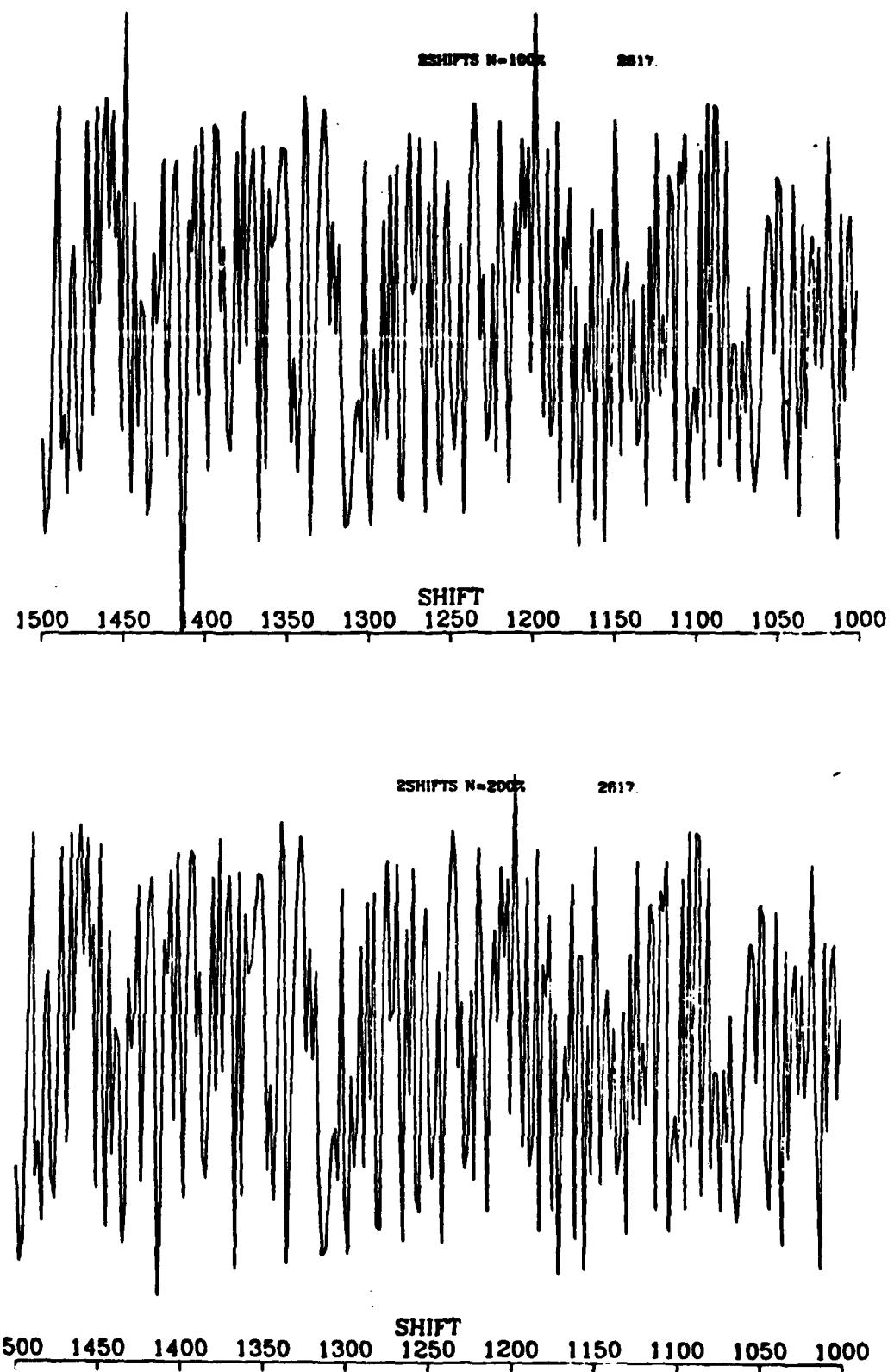


Figure 15. c) Noise level 100 and 200 percent. See Figure 15 a for detailed caption.

of the isotope shifts are limited to a few hertz, however, so the chemical shifts in the pattern-matching routine are constrained to remain very near the 1-D values.

Testing of the software on the experimental 1,1-dimethyltetralin spectrum is proceeding. We found it necessary to scale the experimental values and theoretical values to the same scale, since experimental values incorporate arbitrary scaling factors due to the instrumentation. We are achieving good success in finding the pairs of doublets even in the presence of the extraneous signals. Testing of criteria for determining the presence of a bond is also proceeding. We are investigating the use of spectral intensities, matching locations of maxima and minima in experimental and in theoretical spectra and the tendency of the chemical shifts to move beyond reasonable amounts for an isotope shift.

We are able to produce displays of the 2-D INADEQUATE contour plots on our graphics display raster, either from real or simulated data. We are also able to display and plot traces at any DQF from the data for comparison of real and theoretical spectra. We have found this greatly helpful in analyzing the output of both the simulation and pattern-matching software.

IV. SUMMARY AND CONCLUSIONS

The problem for which we are attempting to devise a solution is a formidable one and may never yield a "final" solution. However, a great deal has been learned during the course of this project which is leading toward a solution. This is evidenced by the fact that most of the carbons in the JP-5 sample were successfully assigned to molecular fragments of five or more carbons. This kind of structural detail has never before been available and should be of considerable value to engineers attempting to devise fuels and build engines for a new generation of aircraft.

It is clear that NMR can supply valuable information about the structure of liquid hydrocarbon fuels. It is also clear that the direction of recent developments in high resolution NMR are conducive to further progress in the area of complex mixture analysis. The variety of pulse and two-dimensional techniques seems to be limitless with new experiments being published in every issue of the relevant journals and various applications of these techniques increasing exponentially.

One of the most important components of a continuation of this project must be increased use of computer assisted data analysis techniques, but computer hardware and software developments are probably the most rapidly advancing technology today. We should be able to exploit this expanding technology as the project advances. The area of computer assisted data analysis and pattern recognition seems particularly fruitful. Commercial NMR spectrometer manufacturers, however, are not moving very rapidly in the directions that directly suit our needs, and we expect to have to continue the development of hardware and software solutions to meet our own needs.

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